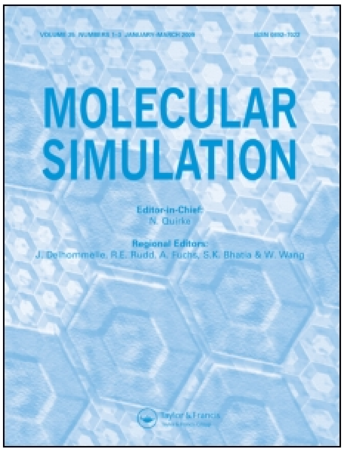

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The Spin-coupled Approach to Electronic Structure

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THE SPIN-COUPLED APPROACH TO ELECTRONIC STRUCTURE

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Recent applications of spin-coupled theory are described, in which accuracy is combined with a clear physical picture of the behaviour of correlated electrons in molecules. Results are presented for gas phase ionic systems (H_2O^{++} and CH^{4+}), to indicate the level of accuracy that can be achieved. The physical pictures that emerge are illustrated by reference to a variety of systems, including CH_2, $C_{10}H_8$, CH_2N_2, VH and Li_4. Opportunities for the future application of spin-coupled valence bond theory to the calculation of interionic potentials in solids are stressed, including techniques analogous to those that have been used to study intermolecular forces.

KEY WORDS: Spin-coupled valence bond theory, correlated electrons, ionic systems, interionic potentials

INTRODUCTION

Most of our fundamental understanding of the electronic structure of molecules and solids is dominated by models such as molecular orbital (MO) theory or band theory in which the electrons move more-or-less independently of one another, experiencing only the time-averaged effects of the electronic repulsions. Such approaches have many serious failings, not least of which is that the Hartree-Fock model breaks down for almost all bond dissociation processes. The inclusion of the effects of electron correlation is essential when calculating potential energy surfaces.

Even in very small molecules, traditional molecular orbital configuration interaction (MO-CI) techniques lead to long lists of configurations which are difficult to interpret. The straightforward *ab initio* application of classical valence bond (VB) theory has always appeared to be an attractive alternative to MO-CI, but the rate of convergence with the number of VB structures is disconcertingly slow.

In this review, we describe spin-coupled theory, which is based on a model of singly-occupied non-orthogonal orbitals with all allowed couplings of the electron spins. The orbitals are fully optimized in the form of completely general linear combinations of atom-centred functions. This approach, which represents the modern form of VB theory, includes from the outset the chemically most important effects of electron correlation. It may be refined further using non-orthogonal CI calculations, but the physical picture is essentially unchanged.

Spin-coupled VB theory is a relatively young technique which has not yet seen direct application to the calculation of interionic potentials in solids. Nonetheless, we can recognize five main reasons why this approach is likely to be of importance in the future for the practical calculation of such potentials:

(1) Spin-coupled VB theory offers an attractive alternative to MO-CI methods for calculations on AB^{n+} and AB^{n-} species, embedded in arrays of point charges chosen to reproduce the Madelung potentials at the relevant crystal sites. The interaction of 'open-shell' ions presents no particular problems, and the method is especially suitable for the calculation of excited-state potentials.

(2) In most – but by no means all – molecular systems, the spin-coupled orbitals turn out to be fairly localized with clearly identifiable atomic parentage. The spin-coupled method is likely to be useful as the basis for calculations on clusters of ions, where the localized character of the orbitals would present distinct advantages [1]. Similar comments apply for models of the local effects of defects in solids.

(3) Spin-coupled VB theory has been very successful in direct calculations of intermolecular forces. The approach provides practical means of avoiding many of the computational problems associated with alternative 'supermolecule' methods. Application of spin-coupled theory to the analogous problem of the interaction between two 'closed-shell' ions would be relatively straightforward.

(4) Spin-coupled theory has already proved itself to be very useful for carrying out critical tests of the accuracy of the kinetic energy, exchange and correlation functionals used in electron gas approaches [2].

(5) In addition to providing a new 'language' for describing *correlated* electrons in molecules and molecular processes, the spin-coupled approach offers a practical framework for developing a highly visual, but accurate, model of correlated electronic motion in crystalline solids. We are currently starting work on this ambitious project.

Accordingly, we review briefly some of the recent applications of our method to small molecules, where the results are both accurate and highly visual. Potential energy curves for several low-lying states of the charge transfer system $C^{4+} + H \rightarrow C^{3+} + H^+$ and of the multiply-charged ion H_2O^{++} are used to demonstrate the accuracy of the method for gas phase ionic systems. Applications of spin-coupled VB theory to intermolecular forces are discussed briefly. Methylene, naphthalene, diazomethane and the VH molecule are chosen as representative examples to illustrate the simplicity of the spin-coupled descriptions that emerge for the behaviour of correlated electrons in molecules. Preliminary results for small metal clusters are also described.

We start with a brief description of the spin-coupled VB formalism. A much more detailed acount is available from a recent specialist review [3].

SPIN-COUPLED VB THEORY

The exact solution Ψ_{SM} of the usual electronic structure problem can be written in the form [4, 5, 6]

$$\Psi_{SM} = \sum_{k=1}^{f_S^N} c_{Sk}\mathscr{A}(\Phi\Theta^N_{SM;k}) \tag{1}$$

in which Φ is an N-electron spatial function which does not possess any particular permutational symmetry; $\mathscr{A}$ is the antisymmetrizing operator, and the c_{SK} may be termed spin-coupling coefficients. The $\Theta^N_{SM;k}$ form a complete set of spin functions for a system of N electrons with total spin S and projection M. For each value of M there are f_S^N linearly-independent spin functions, labelled by the index k, where

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

In spin-coupled theory, we approximate the spatial function $\Phi(r_1, r_2, \ldots, r_N)$ by a product of N distinct non-orthogonal orbitals $\phi_\mu(r_\mu)$:

$$\Psi_{SM} = \sum_{k=1}^{f_S^N} c_{Sk}\mathscr{A}(\phi_1(r_1)\phi_2(r_2)\ldots\phi_N(r_N)\Theta^N_{SM;k}) \tag{3}$$

The spin-coupled orbitals are expanded in a large set of atom-centred basis functions χ_p:

$$\phi_\mu = \sum_p c_{\mu p}\chi_p \tag{4}$$

with no orthogonality constraints whatsoever. All the variational parameters, namely the orbital coefficients $c_{\mu p}$ and the spin-coupling coefficients c_{Sk}, are optimized simultaneously using efficient procedures which utilize the second derivatives of the total energy.

It is important to notice that since the spin-coupled orbitals overlap with one another, the total electron density ρ is not given simply by the sum of the squares of the orbitals. Instead, ρ for a spin-coupled wavefunction is given by an expression of the form

$$\rho = \sum_{\mu,\nu} D(\mu|\nu)\phi_\mu\phi_\nu \tag{5}$$

where $D(\mu|\nu)$ is an element of a normalized spin-less one-electron density matrix, calculated by the spin-coupled programs.

It is often most appropriate to take into account the effects of electron correlation only for the valence electrons. In such cases we usually use restricted Hartree-Fock orbitals or the natural orbitals from a multiconfiguration SCF calculation to describe the 'core' electrons. The spin-coupled wavefunction can then be written:

$$\Psi_{SM} = \sum_{k=1}^{f_S^N} c_{Sk}\mathscr{A}(\psi_1^2\psi_2^2\ldots\psi_n^2\Theta_f^{2n}\phi_1\phi_2\ldots\phi_N\Theta^N_{SM;k}) \tag{6}$$

where the n doubly-occupied orthogonal orbitals ψ_μ describe the 2n core electrons and the N singly-occupied non-orthogonal orbitals ϕ_μ describe the N valence electrons. Θ_f^{2n} corresponds to pairing up the spins of the two core electrons in each orthogonal orbital. The core electrons are acommodated in the doubly-occupied molecular orbitals ψ_μ, and the valence orbitals ϕ_μ are expanded as completely general linear combinations of all the remaining molecular orbitals, regardless of symmetry or occupancy.

The spin-coupled wavefunction already includes a significant degree of electron correlation. The model is sufficiently flexible to describe accurately the key features of potential surfaces, including the positions of minima and barriers, as well as all modes of dissociation. Further refinement, as well as the description of excited states, is achieved by means of non-orthogonal CI calculations, to which we refer as 'spin-coupled VB'.

At convergence, each occupied orbital ϕ_μ satisfies an orbital equation of the type [7]

$$\hat{F}_\mu^{(\mathrm{eff})}\phi_\mu = \varepsilon_\mu \phi_\mu \tag{7}$$

The $\hat{F}_\mu^{(\mathrm{eff})}$ operators are constructed from quantities which depend only on N − 1 electrons. They are all distinct and each of them gives rise to a set of functions $\phi_\mu^{(i)}$ with orbital energies $\varepsilon_\mu^{(i)}$. One of the $\phi_\mu^{(i)}$ corresponds to the occupied orbital already found. The others are 'virtual' solutions that correspond to the motion of one electron in the field of the other N − 1 electrons. Consequently, these orbitals provide very good descriptions of the behaviour of electrons in actual excited states and are very suitable for constructing excited spin-coupled structures.

The final spin-coupled VB wavefunction consists of a linear combination of the spin-coupled configuration and a modest list of excited structures. As mentioned earlier, this step does not change the essential physical picture: the final wavefunction for the ground state is dominated by the spin-coupled configuration for all nuclear geometries. Similar situations hold for excited states.

The spin-coupled VB approach to molecular electronic structure represents the modern development of valence bond theory. The spin-coupled wavefunction can be considered as the natural extension to many-electron systems of the Coulson-Fischer description of H_2 [8]. The spin-coupled method allows us to use large flexible basis sets without introducing any restrictions on the mode of spin coupling, or unphysical constraints on the form of the singly-occupied orbitals or on the overlaps between them. Special cases of the spin-coupled valence bond wavefunction, which may be derived from it by applying various constraints, include the SCF, AMO, classical VB, perfect-pairing GVB, MCSCF and CI wavefunctions.

POTENTIALS FOR IONIC SYSTEMS

The double ionization of a neutral molecule AB might be expected to result in an essentially repulsive $A^+ + B^+$ potential because of the coulombic repulsion. However, we can envisage that short range minima might occur for such systems from the mixing in of $A^{2+} + B$ and $A + B^{2+}$ character. Indeed, many molecular di-cations are stable on the microsecond time scale of a mass spectrometer and a variety of experimental techniques has been used to study them in the gas phase [9].

Prompted by charge transfer and ion-ion coincidence experiments [10], spin-coupled VB theory has been used to study wide regions of the potential surfaces for low-lying triplet and singlet states of H_2O^{++} dissociating to $OH^+ + H^+$, $O + H^+ + H^+$ and $O + H^+ + H$ in various states [11]. The calculations were carried out with compact wavefunctions consisting of just 187 spatial configurations and presented a very clear physical picture of the electronic states, and of various dissociation processes.

In order to give some idea of the reliability of our results for H_2O^{++}, vertical excitation energies are listed in Table 1 for *twenty* electronic states spanning a range of more than 30 eV. The experimental results have been quoted without error bars, which can be quite large: further details concerning the theoretical and experimental work cited in Table 1 can be found in Reference [11]. Spin-coupled VB theory has been used to provide results of a similar high quality for other multiply charged ions, such as the di-cations of methane and ammonia [12].

Another area in which there have been many applications of spin-coupled VB theory to gas phase ionic systems concerns charge transfer collisions between multiply charged atomic ions and neutral targets such as H, He and Li [13, 14, 15]. Such collisions constitute a very important mechanism for establishing the ionization structure of a wide range of terrestrial and astrophysical plasmas. Electron capture preferentially takes place into excited states, which can then emit high energy photons. In addition to cooling the plasma, these photon emissions serve as a useful diagnostic probe for investigating the plasma.

It appears to be a general feature of calculations on charge transfer collisions that it is necessary to consider several states, perhaps 10–15, and all of the avoided crossings between them. In addition to providing a consistently good description of all of these states over the entire range of nuclear separation, it is especially important to describe well the asymptotic splittings, since these determine to a large extent the location and nature of the avoided crossings. Spin-coupled VB theory has been applied to many such systems, with considerable success.

As an example, the spin-coupled VB potential energy curves for low-lying $^2\Sigma^+$ states important in the $C^{4+} + H \rightarrow C^{3+} + H$ system are shown in Figure 1; low-lying $^2\Pi$ and $^2\Delta$ states have also been studied. We list in Table 2 the asymptotic

Table 1 Vertical excitation energies (in eV) for H_2O^+ relative to the mean energy of the two lowest singlet states. Further details concerning the theoretical and experimental work can be found in Ref. 11. The symmetry labels are for the C_s (C_{2v}) point groups.

Spin-coupled valence bond		*Experiment*	*Earlier theoretical studies*		
				ADC(2)	*MO-CI*
$^3A''$	−2.41	−2.2	$^3A''$ ($^3B_1$)	−1.9	−2.1
$^1A'$	−0.73	(0.0)	$^1A'$ ($^1A_1$)	−0.8	−0.7
$^1A''$	0.73		$^1A''$ ($^1B_1$)	0.8	0.7
$^3A''$	2.39		$^3A''$ ($^3A_2$)	2.5	2.3
$^1A''$	4.24		$^1A'$ ($^1A_1$)	4.0	4.3
$^1A'$	4.32	4.8	$^1A''$ ($^1A_2$)	4.4	4.3
$^3A'$	4.84		$^3A'$ ($^3B_2$)	4.4	4.3
$^1A'$	7.26		$^1A'$ ($^1B_2$)	6.6	6.6
$^1A'$	12.68	11.9	$^1A'$ ($^1A_1$)	11.7	11.7
$^3A''$	16.81	16.5	$^3A''$ ($^3B_1$)	16.6	16.4
$^3A'$	19.28		$^3A''$ ($^3A_1$)	18.4	18.1
$^3A'$	24.16		$^3A'$ ($^3B_2$)	22.7	22.2
$^1A''$	24.43	23.3	$^1A''$ ($^1B_1$)	23.6	23.0
$^3A'$	24.58				
$^1A'$	26.12	26.2	$^1A'$ ($^1A_1$)	24.8	26.2
$^1A'$	26.13				
$^3A'$	26.17				
$^3A''$	27.08				
$^3A''$	28.15				
$^1A''$	29.00	30.9	$^1A'$ ($^1B_2$)	30.1	31.0

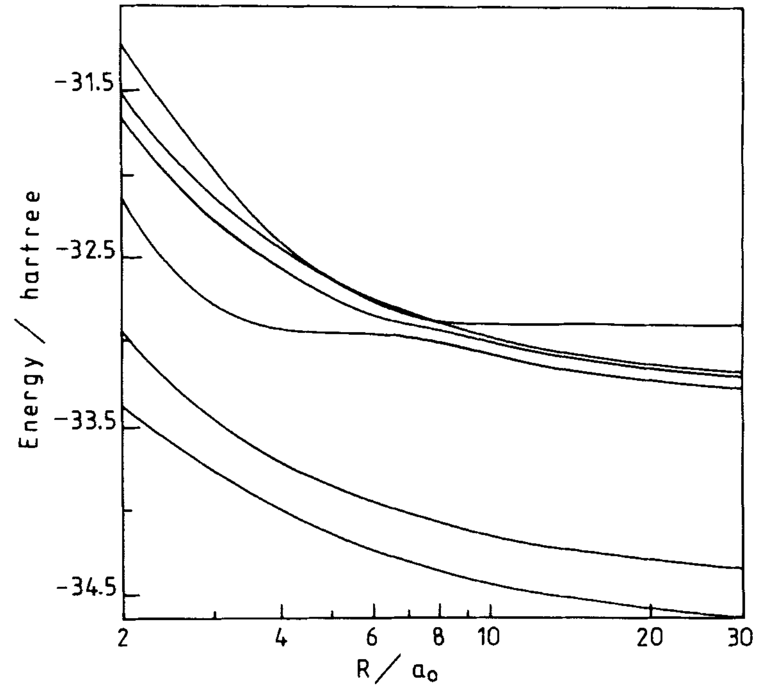


Figure 1 Potential energy curves for low-lying $^2\Sigma^+$ states involved in the $C^{4+} + H \rightarrow C^{3+} + H$ charge transfer process. A logarithmic scale has been used for the nuclear separation R, in order to show more clearly the avoided crossings at short R.

Table 2 Asymptotic energies for the $C^{4+} + H \rightarrow C^{3+} + H^+$ process calculated with different numbers of spatial configurations.

(a)	*$^2\Sigma^+$ states Asymptote*	*Relative energy (in eV)*				
		9	132	157	182	Experiment
	$C^{3+}(2s)+H^+$	−8.10	−8.14	−8.10	−8.09	−8.00
	$C^{3+}(2p)+H^+$	0	0	0	0	0
	$C^{3+}(3s)+H^+$	29.38	29.41	29.45	29.45	29.55
	$C^{3+}(3p)+H^+$	31.56	31.61	31.64	31.65	31.68
	$C^{3+}(3d)+H^+$	32.15	32.19	32.24	32.25	32.28
	$C^{4+} + H(1s)$	42.64	42.68	42.74	42.75	42.88

(b)	$^2\Pi$ states Asymptote	Relative energy (in eV)				
		4	50	63	76	Experiment
	$C^{3+}(2p)+H^+$	−31.57	−31.66	−31.64	−31.64	−31.68
	$C^{3+}(3p)+H^+$	0	0	0	0	0
	$C^{3+}(3d)+H^+$	0.58	0.60	0.62	0.61	0.60

energies for this system, calculated using different numbers of spatial configurations chosen in a systematic fashion. These results [15] demonstrate very clearly the rapid convergence with the number of structures, as well as the high accuracy that can be achieved with very compact spin-coupled VB wavefunctions. This has important consequences for the theoretical study of such charge transfer collisions. We are able to calculate accurate potential curves for all of the relevant states and, because of the compact nature of the wavefunction, it is convenient to evaluate all of the non-adiabatic couplings ($\partial/\partial R$ matrix elements) using finite-difference techniques [15].

As an example of a negative ion, we mention the $X^2\Sigma^+$ ground state of LiH^-, for which we have calculated an accurate potential energy curve using a very compact spin-coupled VB wavefunction consisting of just 55 spatial configurations [16]. The spin-coupled orbitals for this ion are very similar to those of the neutral molecule. The "extra" electron occupies a diffuse non-bonding s-p hybrid orbital localized on lithium and pointing away from the hydrogen atom.

SPIN-COUPLED DESCRIPTIONS OF REPRESENTATIVE SYSTEMS

As we have stressed, in addition to providing accurate results, the spin-coupled VB approach provides a simple orbital picture of the behaviour of *correlated* electrons in molecules. For each of the many classes of molecules that we have studied, the results have been very simple, highly transferable, and often very 'chemical'. In general, spin-coupled calculations on one or two model systems have provided a detailed understanding of a wide range of related molecules and processes. In this Section we discuss the descriptions that emerge for some representative systems, including methylene, naphthalene, diazomethane and the VH molecule.

Methylene

Theoretical interest in methylene (CH_2) has centred on the small energy separation between the triplet ground state ($^3B_1$) and the first excited singlet state ($^1A_1$). The most extensive calculations to date are those of Bauschlicher *et al.* [17] who used large MO-CI wavefunctions with very large basis sets, (including g functions). By comparing with full CI calculations [18], we have shown that very compact spin-coupled VB wavefunctions can provide results of very high accuracy for this splitting [19]. Of more interest to the present discussion is the picture that emerges for the electronic structure of these two states of methylene [19, 20].

Spin-coupled orbitals for the six valence electrons in the $^3B_1$ and $^1A_1$ electronic states of CH_2 are shown in Figures 2 and 3. Although no such preconceptions were imposed in the calculations, it is clear that all the orbitals are fairly localized.

For the triplet ground state of CH_2, ϕ_1 is an sp^2-like orbital which overlaps most strongly with ϕ_2, which is a distorted H(1s) function. Orbitals ϕ_3 and ϕ_4 are the counterparts in the second C—H bond, and may be transformed into ϕ_1 and ϕ_2 by operations of the C_{2v} point group. One of the non-bonding electrons occupies the remaining sp^2-like hybrid, coplanar with the others but pointing away from the two hydrogen atoms. The sixth orbital closely resembles a C(2p) function, pointing perpendicular to the molecular plane. The dominant mode of spin coupling (94.7% of the wavefunction) corresponds to two C—H bonds, with triplet coupling of the spins of the two non-bonding electrons.

For CH_2 ($^1A_1$), ϕ_1 and ϕ_3 are now sp^3-like orbitals which overlap most strongly with the essentially H(1s) functions to which they point. The two remaining sp^3-like hybrids (ϕ_5 and ϕ_6) each accommodate one of the non-bonding electrons. As we would expect, the dominant mode of spin coupling (98.8% of the wavefunction)

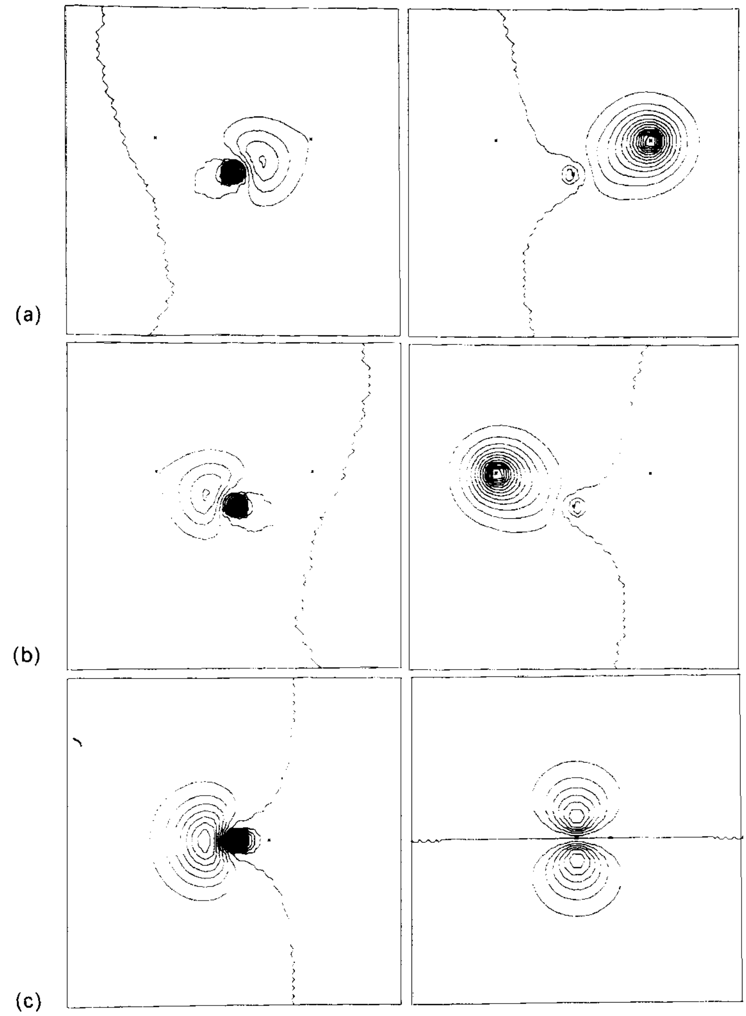


Figure 2 Contour plots of spin-coupled orbitals in the $^3B_1$ ground state of CH_2. Orbitals ϕ_1-ϕ_4 are shown in the molecular plane (σ_v' mirror) and orbitals ϕ_5-ϕ_6 are shown in the σ_v mirror plane. Throughout this review we plot the square modulus of the orbitals, $|\phi_\mu(r)|^2$, and the positions of the nuclei are denoted by crosses.

corresponds to two C—H bonds, with the spins of the two non-bonding electrons coupled to a singlet.

The spin-coupled descriptions of the valence electrons in methylene are remarkably similar to the classical VB picture of sp^2 and sp^3 hybridization. In each case we can identify two equivalent directed covalent bonds formed by the overlap of an sp^x-like hybrid on the heavy atom and a distorted 1s orbital on hydrogen, with singlet coupling of the associated spins. The non-bonding electrons are also accommodated in sp^x-like orbitals or in p orbitals, depending on the overall spatial symmetry of the wavefunction.

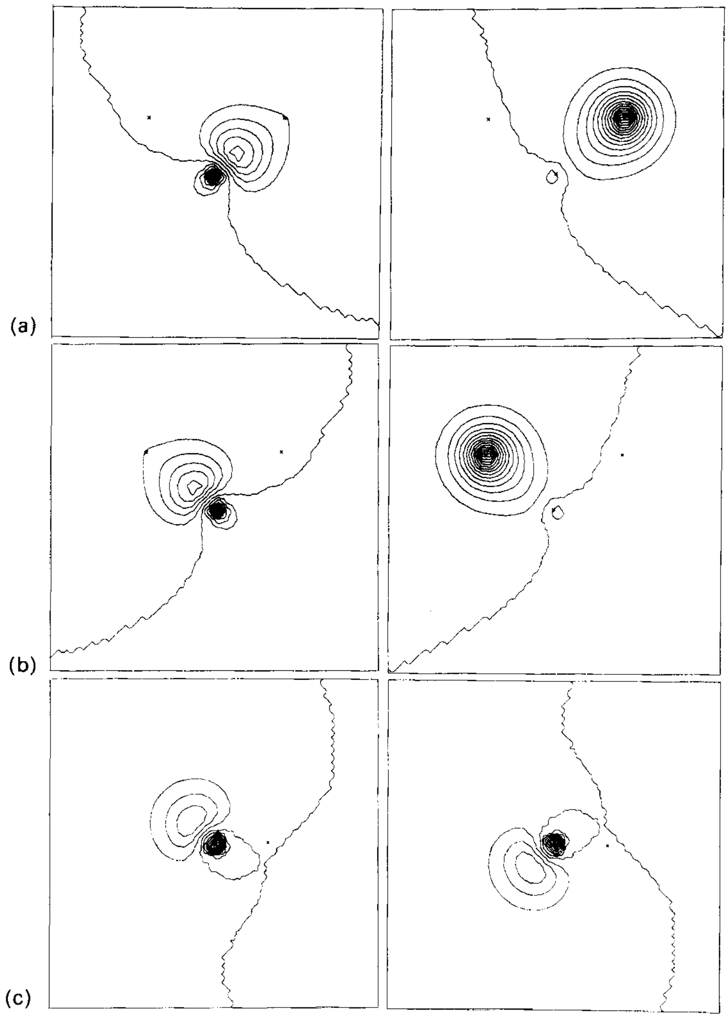


Figure 3 Spin-coupled orbitals in the $^1A_1$ state of CH_2. The views correspond to those in Figure 2.

However, there are also some important differences from the classical VB descriptions of these molecules, not least of which is the accuracy provided by the spin-coupled wavefunction. In addition, all of the orbitals overlap with one another (unless they are orthogonal by symmetry) and show some distortion towards neighbouring centres.

The spin-coupled description of the non-bonding electrons in the $^1A_1$ state differs significantly from the conventional independent-particle MO picture of two electrons in an sp^2-like hybrid in the plane of the molecule. This has dramatic consequences for understanding the reactivity of this species, such as the stereospecificity of cycloaddition reactions with alkenes [19]. In addition, we can envisage a non-least-motion pathway for the $CH_2(^1A_1) + H_2 \rightarrow CH_4$ insertion reaction in which the initial approach of H_2 is with its bond pointing along the direction of one of the non-bonding spin-coupled orbitals. At the same time, the H atom furthest from the CH_2 fragment swings round towards the second sp^3-like non-bonding orbital. Consistent with the experimental observation that singlet methylene reacts with molecular hydrogen with little or no activation energy, our calculations for this reaction pathway find no barrier [21].

The results for methylene indicate some of the insight that can be gained from spin-coupled calculations on such systems, without sacrificing accuracy. The orbital pictures of distorted sp^x-like hybrids and H(1s) functions arose simply by minimizing the total energy, without preconceptions. It is important to stress in this context that the spin-coupled wavefunction is not invariant to arbitrary linear transformations of the orbitals, so that their form is a unique outcome of the calculations.

Naphthalene

Cases for which the conventional wisdom argues most strongly for electrons in delocalized orbitals include the π-electron systems of benzenoid aromatic molecules. However, spin-coupled calculations have now shown that the *correlated* π-type electrons in such molecules are better described in terms of distinct, localized, singly-occupied, non-orthogonal orbitals. There are important contributions to the total wavefunction from various different modes of pairing up the electron spins [22, 23, 24]. As an example, we show in Figure 4 the spin-coupled orbitals at the three unique carbon sites in naphthalene ($C_{10}H_8$) – the remaining spin-coupled orbitals are related to these by symmetry operations of the molecular point group. Each of the ten distinct non-orthogonal orbitals closely resembles a $C(2p_\pi)$ function, slightly distorted towards neighbouring atoms.

The spin-coupled wavefunction for the π-type electrons of $C_{10}H_8$ is dominated by three of the forty-two allowed spin functions for a system with $N = 10$ and $S = 0$ (see Equation (2)). These functions correspond to the three Kekulé structures which can be drawn for this system: it is the important contributions from all three of them which leads to the special stability of this ring system, and we can estimate a resonance energy [25].

Diazomethane

As we have seen, the special stability of benzenoid aromatic molecules arises not from delocalized orbitals but from a distinctly more quantum phenomenon, namely the mode of coupling the electron spins [26]. A particularly striking mode of spin coupling is exhibited by the diazomethane molecule (CH_2N_2) [27], which presents awkward problems for classical valency theories. The usual fashion of representing this molecule is in terms of resonance between a number of zwitterionic and diradical structures:

Diazomethane belongs to a large class of molecules known as 1,3-dipoles which take part in 1,3-dipolar cycloaddition reactions [28] as systems with four π-type electrons. Spin-coupled calculations, concentrating on these π-type electrons, have revealed a very simple, albeit somewhat unexpected picture for the bonding in such molecules [29].

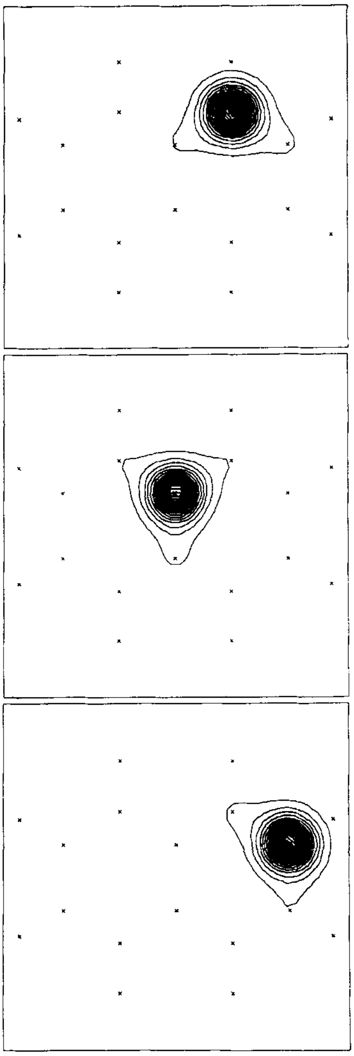


Figure 4 Spin-coupled orbitals ϕ_μ at the unique sites in naphthalene in the plane one unit of atomic distance (≈ 52.9 pm) above the molecular plane.

Each of the four π-type spin-coupled orbitals in diazomethane (see Figure 5) takes the form of a $2p_\pi$ function pointing perpendicular to the molecular plane. Orbital ϕ_1 is essentially localized on carbon, but is distorted towards the central nitrogen atom. Orbitals ϕ_2 and ϕ_3 both stem from the central N atom, but are deformed in very different ways: ϕ_2 is distorted towards C but ϕ_3 shows significant distortion towards the terminal N atom. Orbital ϕ_4 is essentially localized on the terminal N atom, but shows some distortion towards the central N atom. In spite of the fact that ϕ_2 and ϕ_3 stem from the same atom and have a very large overlap (0.785), the corresponding spins are not singlet coupled. Instead, the bonding of the four π electrons in CH_2N_2

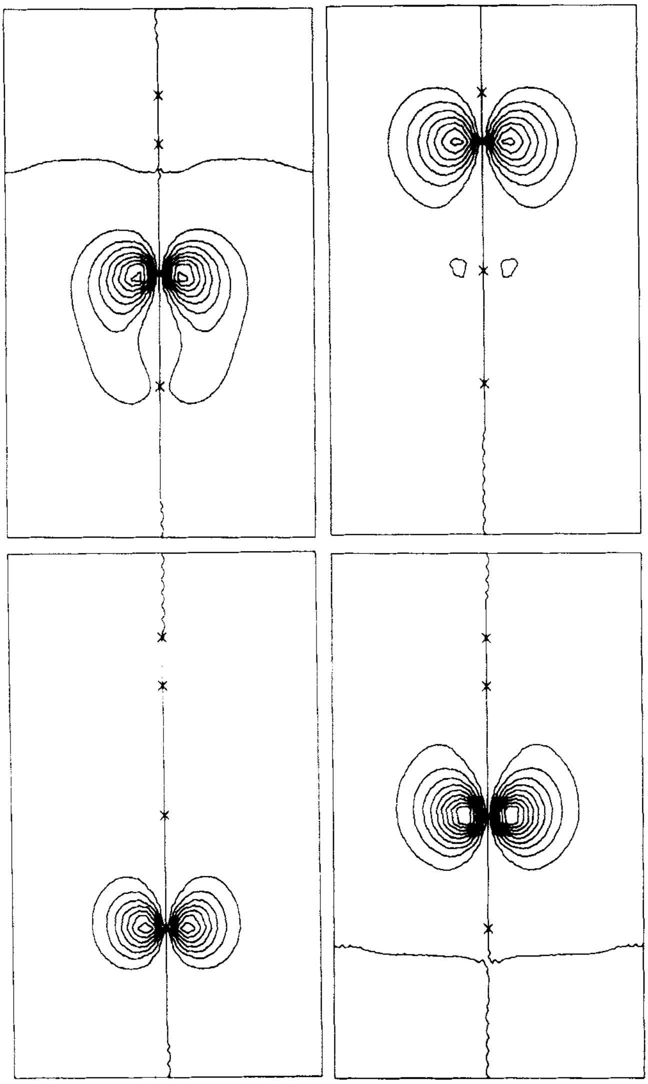


Figure 5 Spin-coupled orbitals for CH_2N_2 in the σ_v mirror plane (perpendicular to the molecular plane).

is dominated by the mode of spin coupling that corresponds to C—N and N—N π-bonds (98.9% of the wavefunction).

If we now include also the bonding in the σ framework, we find that diazomethane has fully-formed C═N and N≡N bonds, so that the central nitrogen atom takes part in *five* two-electron covalent bonds. We use the label "hypervalent" for such a situation, which is the result of subtle electron correlation effects. Our description of the bonding in CH_2N_2 is totally consistent with the geometry and dipole moment of this molecule, and also with the high resilience of the central nitrogen atom to attack by nucleophiles or electrophiles. The only reaction which the central N atom will undergo readily is cleavage of the bond to the carbon atom.

It now seems entirely plausible that our mechanism for the bonding in 1,3-dipoles will also prove to be of direct relevance to understanding the electronic structure of noble gas compounds, as well as the magnetic properties of transition metal oxides.

VH

Progress in characterizing and understanding the bonding to transition metal atoms in low oxidation states has been very slow. This is true even for small molecules containing just one or two transition metal atoms. Such systems present problems for any theoretical method because of subtle electron correlation effects. In addition there is competition between the strong d-d coupling in the separated atoms, and the process of bond formation, which necessitates the breakdown of at least some of this coupling.

An initio spin-coupled calculations are under way for a wide variety of systems, including molecules with metal-hydrogen and metal-metal bonds, and with carbonyl, alkene and phosphine ligands. In all of our calculations, spin-coupled theory is used explicitly for the valence electrons, with the 'core' electrons described by the natural orbitals from a suitable MCSCF wavefunction. More sophisticated calculations will need to take into account the effects of core-valence correlation.

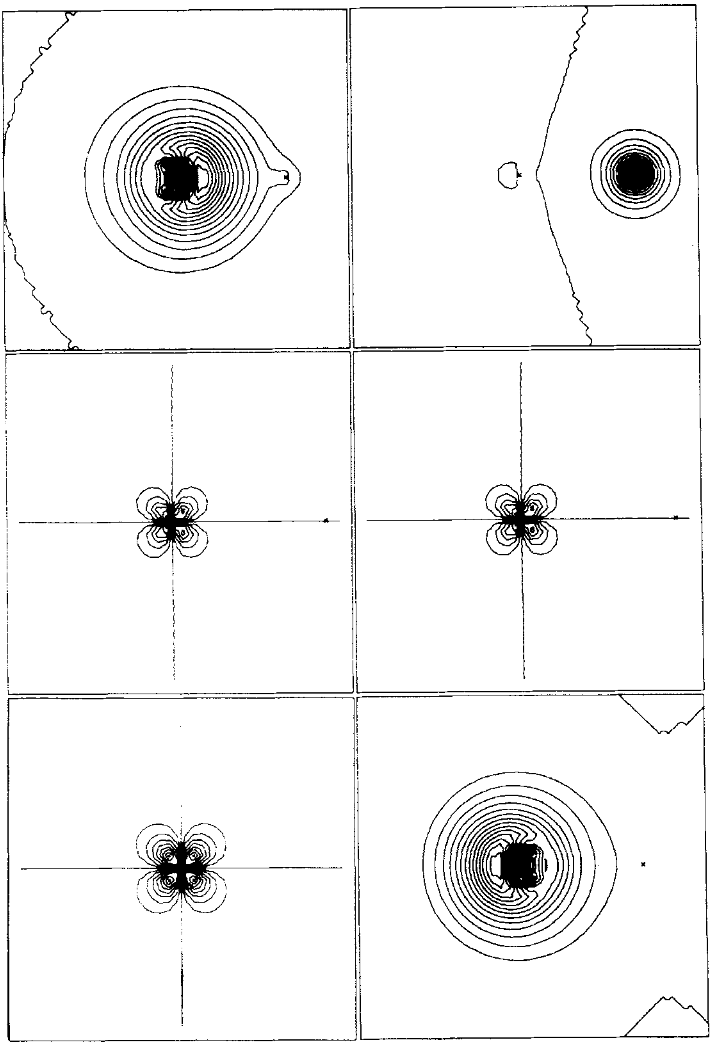
In particular, calculations have been completed for ground and low-lying excited states of MH and MH^+, species (M = Sc – Cr, Y – Mo). We summarize here our findings for the $^5\Delta$ ground states of VH and for VH^+ ($^4\Delta$) [30]. Although these systems are very small by the usual standards of inorganic chemisry, they are already sufficiently complex to exhibit a number of the general features which we have observed so far.

The spin-coupled orbitals for VH ($^5\Delta$) are shown in Figures 6(a) for large R (8 bohr), 6(b) for intermediate R (5 bohr), and 6(c) for R $\approx$ R_e (3.263 bohr). At large R we observe a $4s^2 3d^3$ configuration on vanadium and a 1 s orbital on hydrogen. As the atoms are brought together, the H(1 s) orbital (ϕ_2) distorts slightly towards vanadium. More marked changes occur in the two essentially 4 s orbitals on the transition metal centre. One of them, ϕ_1, distorts towards hydrogen and appears to take on substantial d_z^2 character. The other, ϕ_6, remains esentially the same shape but starts to point away from hydrogen. The remaining orbitals on vanadium change remarkably little.

At still shorter R, ϕ_1 and ϕ_6 take on characteristic forms to which we refer as 'the bonding hybrid' and 'the non-bonding hybrid', respectively. The bonding is linked to the high overlap of orbitals ϕ_1 and ϕ_2, which is a distorted H(1 s) orbital, and to the singlet coupling of the associated spins. The remaining electrons on vanadium have their spins coupled to the highest possible value.

As the atoms are brought together there is a rapid change in the spin-coupling coefficients from values charateristic of separated atoms to values characteristic of the formation of a new covalent bond. The most dramatic changes occur between 8 and 6 bohr, so that the mode of spin coupling at 5 bohr already corresponds to that for the molecular regime.

The spin-coupled description of the $^4\Delta$ ground state of the VH^+ ion closely resembles that for the neutral VH ($^5\Delta$) system, except for the absence of the non-bonding hybrid. A simple and consistent picture is emerging for the bonding in all the MH



(a)

Figure 6 Contour plots of the spin-coupled orbitals $\phi_\mu(r)$ for VH($^5\Delta$): (a) large R, (b) intermediate R and (c) R $\approx$ R_e. The coordinates of the nuclei are z = 0 for V and z = R for H, with the z axis pointing from left to right across the page except for ϕ_5, which is plotted in the plane z = 0.

and MH^+ species we have studied, and it proves possible to formulate simple rules, based on the availability of empty d_z^2 orbitals at large R, to rationalize the ordering of electronic states in these systems. The orbital pictures for high- and low-spin transition metal systems turn out to be very similar.

Our results for the MH and MH^+ diatomics compare favourably with the sophisticated MCPF-based calculations of Langhoff and co-workers [31]. In each case, our calculated states dissociate correctly, give good values of R_e, and are ordered correctly. We believe that the orbital picture provided by spin-coupled theory represents significant progress towards understanding the nature of the bonding to transition metal atoms in low oxidation states.

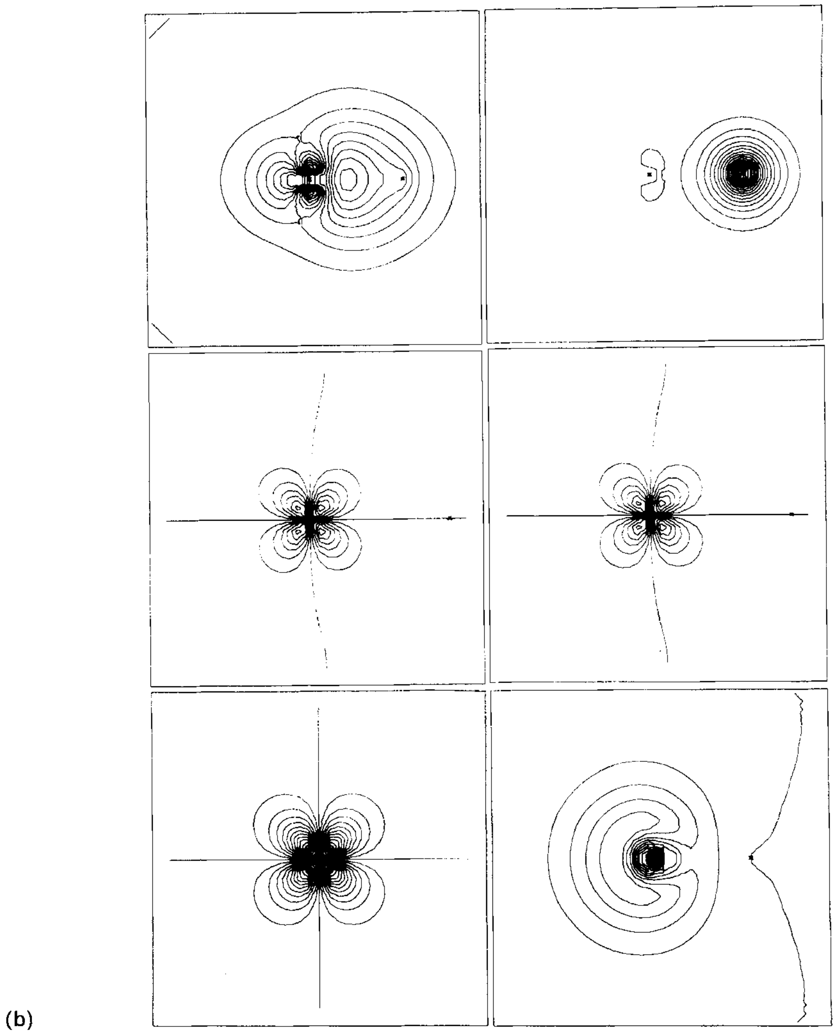


Figure 6 Contour plots of the spin-coupled orbitals $\phi_\mu(r)$ for VH($^5\Delta$): (a) large R, (b) intermediate R and (c) R $\approx$ R_e. The coordinates of the nuclei are z = 0 for V and z = R for H, with the z axis pointing from left to right across the page except for ϕ_5, which is plotted in the plane z = 0.

SMALL LITHIUM CLUSTERS

In a series of calculations for Li_n (n = 2 to 9), Boustani *et al.* [32] found that p functions appear to play an important role in the bonding in alkali metal clusters. According to their geometry optimizations, the smaller clusters (n = 2 to 6) are planar and correspond to distorted sections of the face-centred cubic (111) lattice plane. The larger clusters (n = 7 to 9) appear to be based on distorted tetrahedra with interatomic distances similar to those in the lithium fcc crystal (3.1 Å). Their results

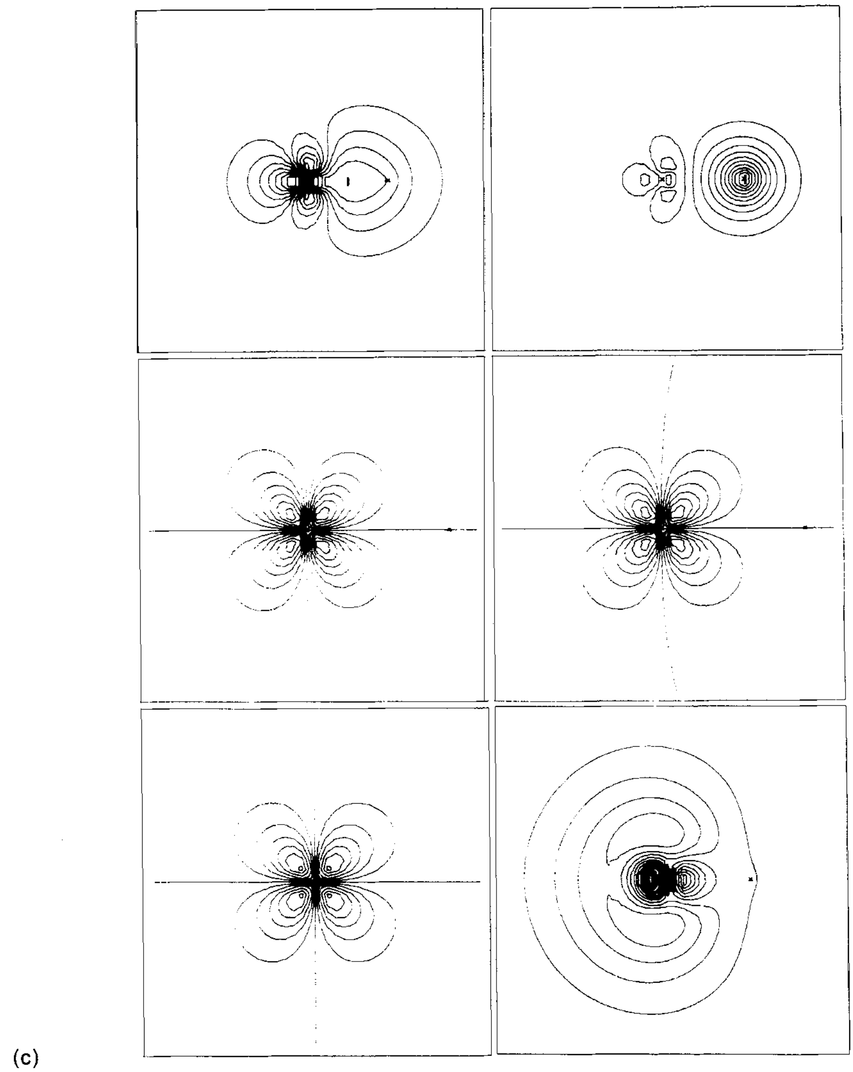


Figure 6 Contour plots of the spin-coupled orbitals $\phi_\mu(r)$ for VH($^5\Delta$): (a) large R, (b) intermediate R and (c) R $\approx$ R_e. The coordinates of the nuclei are z = 0 for V and z = R for H, with the z axis pointing from left to right across the page except for ϕ_5, which is plotted in the plane z = 0.

for small sodium clusters [33] were analogous to those for lithium. The cluster stability increases with nuclearity, although not smoothly, and the geometries show similarities to those of the bulk metals.

It is a general observation for molecules that maxima in the total electron density ρ usually only occur at the positions of the nuclei. The alkali metal clusters turn out to be particularly unusual in that they also exhibit small electron density maxima at other positions. Gatti *et al.* [34], who have analyzed the electron densities of small lithium clusters using the topological partitioning techniques of Bader and co-workers [35], refer to these non-nuclear attractors as "pseudo-atoms". In all of these systems, the lithium atoms appear to be bonded to the pseudo-atoms, rather than directly to one another. The number and types of stationary points in the total electron density ("critical points") appear to be linked to cluster stability, as also is the utilization of p functions. Even Li_2 shows an electron density maximum at the Li-Li midpoint. For the Li_n series studied by Gatti *et al.* [34], the density at the pseudo-atoms increases with cluster size, but it is always much smaller than at the lithium nuclei. Analogous results have been found for sodium clusters [36].

Spin-coupled calculations for a variety of small lithium clusters result in orbital pictures that are very different from those described so far. Instead of taking the usual form of distorted localized functions with clear atomic parentage, the spin-coupled orbitals exhibit maxima on more than one centre and show significant amplitude between the nuclei. As an example, we show in Figure 7 one of the valence spin-coupled orbitals in the Li_4 rhombus at equilibrium geometry. Three other orbitals are related by symmetry to this one, and have the same orbital energy as defined by (7). These orbitals appear to be constructed from the overlap of sp^x-like hybrids on different centres, consistent with the significance attached by previous workers to the utilization of p functions [32, 34]. We have found that increasing the size of the cluster leads to a reduction in the amplitude at the nuclei and to increased localization *between* the nuclei.

The topological partitioning technique mentioned earlier has been extended to deal with electron densities constructed directly from non-orthogonal orbitals (c.f. equation (5)) [37]. For all of the lithium clusters we have studied so far, we find a picture of pseudo-atoms similar to that found by Gatti *et al.* [34]. The electron densities at the pseudo-atoms increase with cluster size. The link between the unusual spin-coupled orbital pictures and the occurrence of non-nuclear maxima in ρ is being pursued further, as well as the clues this work provides to the structure and properties of other metal clusters and possibly of bulk metals.

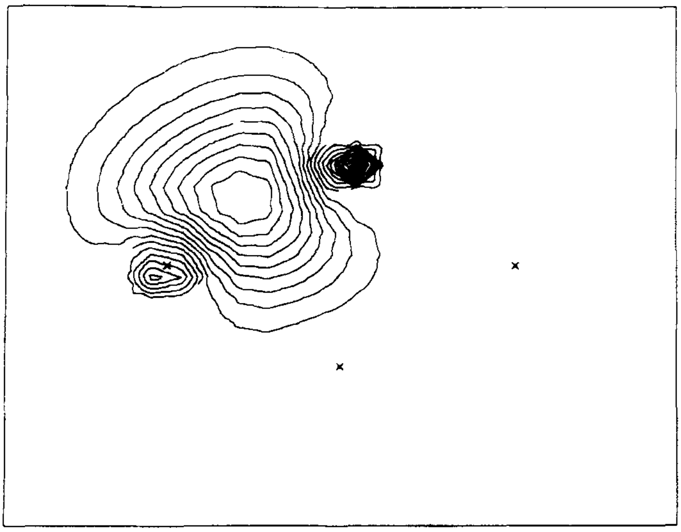


Figure 7 Valence spin-coupled orbital ϕ_1 (in the molecular plane) for the equilibrium geometry of the Li_4 rhombus.

Motivated by the similarities betwen small lithium cluster sand pieces of a lithium surface, spin-coupled calcualtions are also being carried out for $Li_n + H_2$ systems in an attempt to model chemisorption.

INTERMOLECULAR FORCES

The interaction energies between molecules tht do not form chemical bonds are very small. Consequently, approaches to the calculation of intermolecular forces which are based on the role of the individual subsystems are likely to be much more appropriate than 'supermolecule' approaches, except perhaps for the very short-range forces important in high-energy scattering experiments.

One of the most serious problems with supermolecule approaches to the interaction of two molecules A and B is basis set superposition error (BSSE), whereby basis functions stemming from molecule A improve the description of molecule B. No satisfactory correction exists for BSSE, the presence of which leads to results which are physically unreliable and difficult to interpret. A further problem relates to size consistency: the electron correlation energy calculated by most MO-CI techniques does not scale correctly with the number of correlated electrons.

Consider instead the interaction of two molecules A and B described by SCF MO theory wavefunctions Φ_A^0 and Φ_B^0, respectively. These are constructed from occupied orbitals a_i^0 and b_i^0 which are expanded only in terms of basis functions stemming from the particular molecule. If we now use these orbitals to describe the interactions of A and B, without resorting to orthogonalization, then it is clear that the problems of BSSE are completely avoided provided that we do not allow for charge transfer effects.

We now introduce 'excited' orbitals a_i' and b_i', satisfying Brillouin's theorem, which are used to construct wavefunctions Φ_A' and Φ_B' for 'pseudo-states' of A and B. These are not spectroscopic states, but their matrix elements with the ground state wavefunctions determine the response of the subsystems to an external perturbation, such as an electric field. For example, in calculations of He. . .HF interactions [38], the pseudo-state orbitals were obtained by means of a finite field technique.

The following classes of configurations are included in the VB calculations, where curly brackets { } represent multiplication by a spin function and complete antisymmetrization:

(1) $\{\Phi_A^0 \Phi_B^0\}$. For large separations R these describe electrostatic interactions.

(2) $\{\Phi_A^0 \Phi_B'\}$ and $\{\Phi_A' \Phi_B^0\}$. In the long-range limit these account for polarization effects.

(3) $\{\Phi_A' \Phi_B'\}$. For large R these describe the dispersion energy.

In order to account for charge transfer effects of the form A^+B^-, separate calculations are needed for the isolated A^+ and B^- systems so as to produce orbitals a_i^{+0}, $a_i^{+\prime}$, b_i^{-0} and $b_i^{-\prime}$. The key to the description of charge transfer effects without introducing BSSE is the inclusion in the VB wavefunction of structures such as $\{\Phi_A^{+0} \Phi_B^{-0}\}$.

Intramolecular correlation can be included in a size consistent manner, without introducing BSSE, provided all excitations are from occupied orbitals to virtual orbitals on the same subsystem. A more promising approach is to use spin-coupled VB theory for the two fragments, but allowing the orbitals to 'relax' at each interfragment separation. In order to avoid BSSE, it is important to expand the occupied and virtual orbitals only in terms of basis functions stemming from one or other of the fragments. Work using this strategy is in progress for several systems.

The purpose of this short Section has been to give some idea of the way in which VB methods can be used to calculate intermolecular forces. The calculations can be designed in such a way that not only are they size consistent, but the effects of BSSE are eliminated. Further details, as well as a discussion of perturbation theory approaches, can be found in a recent review [31]. The application of the techniques mentioned here to the calculations of interionic potentials in solids would be relatively straightforward, and this is a particularly promising avenue for future work.

FINAL REMARKS

The spin-coupled VB approach combines high accuracy with a clear physical picture of the *correlated* electronic structure of molecules. The outlook for future work is very promising indeed, not only for a wide range of molecular systems but also for crystalline solids. In particular, it is to be hoped that spin-coupled VB theory will soon see a variety of direct applications to the practical calculation of potentials in solids.

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