

# the newsletter of CCP1 collaborative computational project 1

## Obituary: Joseph Gerratt

(1938-1997)

Joe Gerratt died on 16<sup>th</sup> October 1997, aged 59, from an unsuspected cancer. He left friends, colleagues and the world scientific community in deep sadness and shock. It is difficult to say what struck most about his personality. Beyond his scientific culture, it was certainly his open-hearted nature and sense of humour, and his style of approaching reality with such a large view. Never refusing diversity, his interest for the new, ideas and intuitions, formed the basis of his soul and intelligence. Heart, soul, intelligence were always involved and Joe was absolutely unique in transmitting love and enthusiasm for research and science. His last lesson is the courage and the dignity with which he faced up to "the last tragic news and the last days".

Joe started his research career with some work that subsequently turned out to be very important indeed: he showed how to calculate *analytically* gradients and higher derivatives of the energy of a molecule with respect to nuclear coordinates [1]. This has now become an enormous undertaking world-wide. The calculation of such gradients is now routine, using methods clearly descended from those he established.

After this very successful debut, his primary interest was in the theoretical study of molecular electronic structure and chemical bonding. He believed that in order to make sense of the enormous variety of bonds that occur in chemistry, we need a description that not only furnishes accurate results, but which also provides us with a convincing physical model, *i.e.* a model which affords us our all-important *insight* into electronic structure and bonding. He was convinced that Quantum Chemistry had concentrated almost exclusively upon a continuous refinement of the accuracy of the theory – to the extent, aided of course by the enormous computer power now available, of producing results of great precision, but of such complexity that our crucial chemical and physical insight is often all but completely obliterated.

Joe developed the spin-coupled theory [2] as an attempt to incorporate his vision of chemistry into a precise, rigorous, quantum mechanical approach much closer to the physics and chemistry of the problem and, moreover, able to preserve our vital insight. He did not lose sight of the fact that such a description, if it is to carry any conviction, must also provide reliable numerical results which, in addition, must be open to refinement if one so wishes. He was also a great teacher and a good raconteur and sometimes took up the challenge of explaining his view of the chemical bond to a discerning audience of non-specialists. It was with one of those opportunities that he liked to express himself in this way:

"Electrons possess a property known as 'spin'. This is equivalent to the possession by each electron of a small magnet. A chemical bond consists of a pair of electrons in which the spins of the two electrons are aligned anti-parallel to each other, *i.e.* in which the spins are *paired*. By concentrating on all the different possible ways of pairing the electron spins in a molecule, we are led to a complete reformulation of the problem: Each possible mode of pairing of these tiny magnets reveals something about the behaviour of the electrons. Furthermore, *changes* in the contributions of each mode of pairing show us clearly how chemical bonds form and break – and how chemical reaction is progressing. In this way an enormous amount of new light is cast upon chemical reactivity and the properties of molecules".

Of course all of this rests on the concept of "*spin-coupled orbitals*", whose essential characteristics are those of being singly occupied and free to overlap; it is in fact in the overlap between the wavefunctions of the participating atoms that lies the origin of the crucial exchange effect. The great success of *Spin-Coupled Theory*, which can be regarded as a *Modern Form of VB Theory*, is that, much as in the MO theory, the orbitals are expanded in a basis set and then fully optimised at each internuclear distance. It is in this way that *re-hybridisation* is naturally incorporated into the method. The full simultaneous optimisation of orbitals and spin-coupling coefficients is the incomparable advantage of the spin-coupled theory. It is this peculiarity which provides the spin-coupled wavefunction with that *visual* direct interpretability of bond formation and bond breaking processes.

If it is true that this revival of VB theory had its birth almost simultaneously in the USA, thanks to the *Generalised Valence Bond* approach developed by Goddard [3], Joe's work is by all means original and fully independent. He attacked the problem and went deep into it with absolute commitment. He was not afraid of getting involved in a difficult and risky undertaking, so he took up the challenge to derive first the expressions of the second derivatives of the spin-coupled energy with respect to orbitals, spin-coupling coefficients and the mixed terms in the framework of the symmetric group, and then he wrote the full code by himself. Another originality of Joe's formulation of spin-coupled theory, was his ability to formulate the equations from which to generate also sets of *virtual* orbitals [4]. Their use to build a *non-orthogonal CI* wavefunction gave rise to the *Spin-Coupled Valence Bond* method which has proved extremely powerful to describe excited states with great accuracy, sometimes even stretching over a range of more than 40 eV.

Later developments have brought us to the currently existing three main strategies for optimising spin-coupled wavefunctions. In the first one, the symmetric group strategy is exploited, and the approach has been extended to include the optimisation of the coefficients also of a set of doubly occupied orbitals – *inactive orbitals* [5]. The second approach expands the spin-coupled wavefunction in Slater determinants constructed from non-orthogonal orbitals [6]. Calculations have been carried out with this strategy for up to fourteen active electrons [7]. This approach has also recently been extended to include optimisation of inactive electrons [8]. The third scheme, known as CASVB [9], may be used either to generate compact representations of CASSCF wavefunctions or to perform fully-variational optimization of various types of modern VB wavefunction, such as spin-coupled and multiconfiguration spin-coupled wavefunctions.

All of these old and new developments are really the ripe fruits of Joe's labours, opening the broad perspective of newer applications of VB theory which we are sure will continue to innovate the whole area of computational chemistry. The reasons for believing this, sharing Joe's enthusiasm, is that there are already many things that we have learnt from spin-coupled theory: we found aspects of which we could not have such a clear view before.

One example, which first brought spin-coupled theory to wide public attention was a paper in *Nature* [10] about the electronic structure of the benzene molecule, the quintessential 'aromatic' molecule in chemistry, where the spin-coupled results overturned 30-40 years' firmly-held convictions in Quantum Chemistry about *aromaticity*. Furthermore, the effect of substituents on the energy and the electron distribution of the arenium intermediates in aromatic electrophilic substitutions was borne out in a particularly clear and visual way [11,12]. If *aromaticity* was typically described in benzene and in the related systems, *antiaromaticity* appeared as a character connected to the formation of a triplet spin state from a pair of electrons in two distinct orbitals of the C<sub>4</sub> ring in cyclobutadiene [13]. In addition to

characteristic orbitals, it is the peculiar scheme of spin coupling – two triplet pairs coupled to an overall singlet – which furnishes the interpretative key of antiaromaticity in this system. The generalisation of this picture came from calculations on the sequence of systems where two hydrogen atoms of the  $C_4$  unit are substituted with methylene groups or further cyclobutadiene units. The generalisation of these ideas led to the *antiferromagnetic spin couplings* model exemplified in a study on cyclobutadiene chains [14].

The theoretical interpretation of reaction mechanisms of cycloaddition reactions started long ago and was one of the last subjects which attracted Joe's interest. The first spin-coupled attempts were the description of  $CH_2$  and of its reaction with molecular hydrogen to form methane [15] and with ethene to form cyclopropane [16]. Here it was interesting to note that along the reaction path there is a region in which the orbitals originally centred on ethene deform substantially and are delocalised towards the more electrophilic  $CH_2$ . There is a moment where it is easy to detect the action of a hook or claw, and the term 'chelotropic' appears quite appropriate for the orbital picture furnished by the spin-coupled wavefunction. A recent study of the ethene+ethene addition reaction [17] is another example of how spin-coupled theory is particularly useful in the description of both the qualitative changes of the orbitals and of the spin recoupling processes accompanying such a reaction.

It would have been impossible without spin-coupled calculations to reach such compelling evidence to suggest that the much familiar octet rule for main group elements should be demoted in favour of the so-called *democracy principle*, according to which any valence electron can participate in chemical bonding, depending only on the availability of sufficient energetic incentives [18]. It was in his last days that Joe was updating the final version of a new paper on N-S compounds: it was for  $N_2S_2$  that a spin-coupled study revealed with extraordinary clarity that this molecule has the character of a singlet radical [19]. The two N atoms at the two opposite vertices of the square bear a negative charge, while the two S atoms bear a complementary positive charge: The electronic structure of the six electron  $\pi$  system is described in this model by two orbitals on each N paired to form singlets and by two orbitals highly localised on each S, but possessing a nodal surface, roughly half way between the two S atoms; the spins associated with these two orbitals are again coupled to form a singlet.

The subject of *collisions* also received Joe's attention. Here it was the  $L^2$  R-Matrix method which stimulated his enthusiasm, as shown by very interesting and innovative studies on the energy dependence of rotation-vibration inelastic cross sections for  $^4He+H_2$  [20], his development of the R-Matrix theory of charge transfer processes [21], and the work on resonances in collisions of He and  $H_2CO$  [22].

This is just a short overview of Joe's work. On behalf of all other collaborators and students, we express our conviction that Joe will always be here inspiring our hands and our minds as we do science – a science which we would like to carry out in his style. A style characterised by high standards and a clarity of interpretation which in itself represented a renewed vision of knowledge, a unifying cultural approach so urgent and necessary in these days of overspecialisation that can make it very difficult, if not impossible, to understand one another.

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Although most quantum chemists would associate the name of the late Joe Gerratt with the 'renaissance' of valence bond theory largely brought about by the spin-coupled approach he introduced, this is just one of a number of considerable achievements made by this remarkable scientist.

In his graduate work, with I.M. Mills, he pioneered the analytic evaluation of force constants and energy derivative which has enabled detailed studies of potential energy hypersurfaces by quantum chemical methods. In his volume tracing the development of *ab initio* methods in quantum chemistry, Schaefer writes "... the Gerratt and Mills paper has become a genuine classic in the history of molecular electronic structure theory".

Joe's main interests included the calculation of potential energy curves and surfaces, the description of intermolecular forces and the explanation of the nature of chemical bonding. Having recognized at an early stage the inadequacies of the Hartree-Fock molecular orbital theory, he advocated the use of valence bond theory, which in another landmark paper, published in 1971, he cast into its 'modern' form. With an encyclopaedic knowledge of the work of pre-war pioneers, such as Heitler and van Vleck, he laid the foundations of a practical *ab initio* valence bond theory. His theory of spin-coupled wave functions employed the spin permutation group and the symmetric group to construct spin eigenvalues. He built on the work of Racah, Wigner, Kotani, Serber, Jahn, Löwdin, Kaplan and others in developing his general theory, which, in more recent years, has seen a wide range of applications. The spin-coupled approach introduces a simple intuitive picture of chemical bonding contained within an *ab initio* wavefunction which already incorporates the most important electron correlation effects. The quality of the spin-coupled wavefunction remains uniform over wide ranges of molecular geometries which, together with its straightforward interpretability, makes it particularly suitable for the description of the electronic mechanisms of chemical reactions. The well-known spin-coupled description of benzene which reinstated the classical valence bond picture in terms of Kekulé and Dewar resonance structures can now be found on the pages of several recognized textbooks.

Joe was always a source of radical ideas, which he was pursuing with remarkable persistence till his very last days. His most recent unfinished project was related to the application of the unitary group approach to the calculation of spin-coupled wavefunctions and the initial derivations indicated that this might have been the most efficient way of attacking the nonorthogonality problem.

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