



## MAGIC: an integrated computational environment for the modelling of heavy-atom chemistry

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The nuclear industry has enormous challenges to address in understanding its waste products and their safe disposal. It is extremely expensive and difficult to work with such waste products. As computational chemistry has made so many advances in the last 30 years, the question arises as to whether it can start to answer some of the basic questions. It was in this context that British Nuclear Fuels plc approached the quantum chemistry group at the University of Cambridge. After initial considerations, it was decided to write an entirely new quantum chemistry package to address these fundamental problems. The MAGIC|| program has been written to model as accurately as possible the properties of heavy-atom (in particular, actinide) complexes in realistic environments. Major requirements were the need to include relativistic effects for which several investigations have been carried out by quantum chemists in recent years. A severe difficulty is the high angular momentum of the occupied orbitals in the actinides. It was also believed that it was very important to include the effects of electron correlation. Again much progress has been made by quantum chemists with this problem. Therefore this code was written to take into account all these advances in a simple enough way that calculations on realistic systems are possible. The program is the result of a collaboration between British Nuclear Fuels plc and the University of Cambridge. The program has been developed with a view to making the implementation of new ideas as straightforward as possible. Hence, the code has a simple modular structure. Individual modules may of course be combined in a script to run more complicated procedures, such as a self-consistent field (SCF) procedure. The aim of such an approach is to maximize the time spent in the science compared with that spent interfacing with the computer code. For the end user a simple graphical user interface through Cerius<sup>2</sup> is provided. Standard features of the input may be selected easily from individual menus for each module. It is also possible to access more advanced features. Comprehensive help facilities are available within the interface. Use of the visualization tools helps not only to see the results of calculations on large molecules more clearly, but also to present them in a concise and clear way. The program has been developed on an SG workstation, but it has been extended to run in parallel on a Cray T3E. This paper is the basic paper which describes in detail the philosophy, science and implementation of the MAGIC project. At the end, sample calculations are reported. Furthermore suggestions are made about how this program may, even at this stage, be used to address problems with actinides in the nuclear industry. In order to place the development of the MAGIC project in context and to make adequate recognition of the contribution of others, this article contains considerable material of a review nature, a brief history of the development of quantum chemistry and density function theory, the

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|| The name MAGIC has no direct meaning. It is simply a memorable name made up from some of the initials of the original program developers.

treatment of core electrons and relativistic effects, the evaluation of integrals, the treatment of solvent effects and the convergence of the SCF iterations. All are written with calculations on actinide complexes as the ultimate goal.

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### 1. Introduction to the MAGIC project

The use of nuclear fission for the generation of energy presently accounts for 25–30% of the world's energy supply [1]. This creates a problem, however, in what to do with the spent nuclear fuel. One solution is simply to dispose of it. A more elegant and environmentally aware solution, however, is to reprocess it to extract materials of use. This will clearly involve recovery of any uranium-235, which forms the basis of the fission process itself. It will also include extraction of plutonium, which is formed in the reactor from uranium-238.

There are a number of advantages to recycling in this way. As the uranium-235 content of naturally occurring uranium ore is very low, the fuel is enriched before being used. This keeps the size of reactors down and means that the fuel has to be changed less often. However, such enrichment, typically by diffusion or centrifuge, is expensive. In the spent fuel the uranium-235 content is typically higher than in nature and so less enrichment is necessary. Hence the cost of producing fresh fuel is reduced. Another advantage is in the conservation of resources, which has become a major topic in recent years. This may also be extended to the use of ex-military material, where the alternative is simply a difficult disposal procedure. Finally, one easy way of restricting access to plutonium is to store it in a mixed fuel; it is a straightforward procedure to generate such a mixed fuel within the reprocessing cycle.

Spent nuclear fuel consists of actinide elements and their fission products. The first step in reprocessing is therefore to separate uranium and plutonium from the fission products. This involves a liquid separation between aqueous and organic phases. The spent nuclear fuel is first dissolved in nitric acid. Any insoluble material can be filtered at this stage. The rest is passed through a mixture of an organic solvent, typically tri-*n*-butylphosphate (TBP) in odourless kerosene, and water. The important uranyl and plutonyl nitrates complex with the TBP and are extracted in the organic phase. Most of the other nitrates simply dissolve in the water and are extracted in the aqueous phase. In this way the uranium and plutonium may be separated, together with some contaminants. The next stage is to separate the uranium from the plutonium. This may be achieved by changing the oxidation state of the plutonium. For example, U(IV) in hydrazine reduces the extractable Pu(IV) complex to the practically inextractable Pu(III) complex.

Once the uranyl nitrate has been separated, it is heated to produce uranium trioxide, which may be subsequently reduced to give uranium dioxide. It is this which provides the basic fuel for the reactor. Before use, however, it needs to be enriched. For this reason it is converted to uranium hexafluoride; this is a convenient choice because it is gaseous under the conditions of the diffusion experiment and fluorine has only one isotope. It is subsequently converted to uranium metal or back to uranium dioxide for use in the reactor. The plutonyl nitrate may also be heated to produce plutonium dioxide but, because of the presence of impurities, conversion to plutonium oxalate and heating to give the dioxide is more typical.

The metal nitrates, which were extracted in the aqueous phase, must now be disposed of. These are classified as high-level waste. They are denitrated and vitrified ready for long-term storage. Material from the recycling process, for example cladding materials from the fuel rods, is encapsulated in cement. Other low-level waste is simply buried in vaults.

It is clear that a good understanding of the chemistry of these systems can be used in a number of areas. In the area of liquid separation a number of criteria need to be satisfied for a good extractant. These include a high distribution ratio for uranyl and plutonyl nitrates, which is sensitive to the acidity, different affinities for different actinide elements, in particular uranium and plutonium, negligible affinity for the fission products, stability to chemical and radiolytic breakdown, and low toxicity, with harmless degradation products which are simple to dispose of. We believe that quantum chemistry can be used to model some of the molecules; in particular the change in their high-energy properties in different environments can now be studied. In combination with experiment, such understanding can lead to the use of improved extraction methods. The potential saving involved, because of the need for less

experimental work, is considerable. Hence it may be possible to extract uranium and plutonium more efficiently or, for example, to extract other actinide elements effectively. Another example might be to look for an extractant for the heat-releasing elements (caesium and strontium) which cause problems later in waste storage, or for technetium which affects the efficiency of the uranium–plutonium separation.

A second area in which theoretical chemistry could be used is in describing the final waste storage procedure. It is important to engineer properties of the glasses in which the high-level waste is vitrified. For example, they must incorporate the maximum amount of waste material. They should be sufficiently reactive that they incorporate the waste but also durable so that they do not need to be maintained over long periods of time. With a good theoretical model, such properties may be predicted as well as the likely effects of waste incorporation on the glass structure. Similarly, in the case of intermediate-level waste, the cement properties such as chemical stability and leach behaviour may be predicted. Theoretical chemistry may provide parameters for a more reasonable model of the system, or in some cases it may even provide the model.

Having established an outline of the types of application to be studied, a choice was then made about how to do the calculations. The easiest (and cheapest in the short term) route would have been to use an existing computer package. The first problem with this is that, although such programs have been widely applied to elements in the first and second rows of the periodic table, applications with actinide elements are still rare. Even where available, they tend to be detailed examinations of small molecules in the gas phase, rather than the complex systems to be studied here. Also it was not possible to find a program which would satisfy all the needs of the project. Even if it had been possible, it is inevitable that such a program would need to be refined or extended and this is often difficult to do. Part of the reason for this is that, as quantum chemistry improved in the period 1970–1990, so many models were tried with no definite conclusion over an optimum choice. The programs therefore grew to incorporate many possible models and this led to much confusion. For the MAGIC project, therefore, a choice was made about the basic model that would be used.

Having made this choice we also had to address the problems of the robustness of the program. This refers not only to how the program executes but also, for example, in the ease with which it may be moved between different computer platforms. Ways in which we have done this include making the code structure as simple and short as possible. Where possible, external mathematical library routines are used. In starting from scratch we have also been able to decide on the modular format of the program which helps not only to understand the running of the existing procedure, but also to add extra functionality. With such a code it is also important that it should be straightforward to run. This is addressed by the use of the Cerius<sup>2</sup> package by Molecular Simulations Inc., to which MAGIC has been interfaced, although the program can be run without it. In this way, the development effort should be directed to improvement in the scientific model and not to attempts to understand the existing computer science.

In choosing the scientific model we had to consider both the complex systems that we wish to examine and the properties that can reasonably be predicted. It is clear that this should be a relativistic model. A full Dirac–Fock four-component analysis is rejected owing to the size and complexity of our systems. A two-component analysis is therefore favoured, although as it is not clear whether the Douglas–Kroll (DK) [2] treatment or the Chang–Pelissier–Durand (CPD) [3] treatment is more reliable, we have included both. Even these methods, however, are expensive compared with the

use of relativistic effective core potentials, which form the basis of our initial model. Should we be unable to make reliable predictions based on these, and a two-component model is a demonstrable improvement, then the basic model will be changed.

As much of this chemistry takes place in the liquid phase, solvent modelling is important. The simplest approach is to use a cavity model [4] where the liquid is a bulk continuum with a fixed dielectric constant. A multipole expansion of the solute is performed and it is through this that the effect of the solvent is felt. Again our philosophy is to use the simplest reasonable model for our systems of interest, which we feel is an elliptical cavity and a quadrupole expansion. Many refinements are possible within this model, for example sophisticated cavity shapes and higher multipole expansions, but before inclusion in the basic model they would have to be demonstrably better than our existing model. It is more likely that our major approximation lies in not allowing specific interaction between the solvent molecules and the solute. One way to remove this is to perform a calculation on a small collection of solute and solvent molecules using the quantum-mechanical model. This soon becomes too expensive and so we are examining the use of mixed quantum-mechanical–molecular-mechanical [5] models.

The choice of a quantum-mechanical method is crucial to the predictive success of the entire model. We believe that it is important to include electron correlation in the model. The high-level correlated techniques, such as the configuration interaction (CI) [6] or coupled-cluster (CC) [7] methods, are, however, too expensive when applied to such large systems. Also, although they may be conceptually straightforward, their implementation is often much less so. We have therefore chosen to use density functional theory (DFT) [8].

For direct comparison with other methods we have chosen to use a Kohn–Sham procedure in our implementation of DFT. There are a number of different density functionals to choose from, each with its particular advantages over others. As it is difficult to choose just one possibility, we have included both the local density approximation and the Becke–Lee–Yang–Parr (BLYP) functional, although the latter is not part of our standard model [9, 10].

The intensive two-electron integral computation is included in the model through a three-centre approximation. The integrals are evaluated directly, that is as required, without the need for their storage. This introduces the use of an auxiliary basis set. A four-centre integral routine is currently under development and offers the opportunity of greater comparison with existing calculations. It will also be used to verify the accuracy of the auxiliary basis sets.

Within the model it is possible to make a number of further approximations in situations where we know *a priori* the values of certain quantities. For example, we may well know that many elements of a particular matrix are vanishingly small. It may then become possible to save computational time by skipping their calculation. Where it can be shown that such an approximation has no effect on the quoted accuracy of the final computed properties, it is allowed. We have successfully used such approximations in both the two-electron and the DFT routines.

Although it is possible to calculate simple properties of the systems, that is a Mulliken population and charge analysis, dipole and quadrupole moments, emphasis has been placed on the use of external modules. Thus it is of advantage to use the existing property analysis tools in a package like Cerius<sup>2</sup> where available and write specific modules to evaluate those properties which are not.

## 2. Quantum chemistry

In the year of writing (1999), quantum chemistry has been recognized through the award of the Nobel Prize in Chemistry to W. A. Kohn and J. A. Pople [11] jointly. On any basis therefore the field is recognized not simply for its ability to solve the quantum-mechanical equations to a good degree of approximation for any molecule but also for the fact this field can undertake calculations of real benefit to the community. We start by outlining how quantum chemistry can reach into the study of actinides and their complexes.

Since 1926, theoretical scientists have been trying to solve Schrodinger's [12] equation for molecular systems. An incomplete historical survey of work which has stood the test of time as far as this project is concerned would include the following:

- (1) the hydrogen molecule by James and Coolidge [13] in the 1930s;
- (2) molecular orbital (MO) theory due largely to Mulliken [14] and Slater [15];
- (3) self-consistent field (SCF) theory due to Hartree [16] and Fock [17];
- (4) the introduction of Gaussian basis functions by Boys [18];
- (5) the presentation in 1964 by Nieuwpoort [19] of *ab initio* calculations on metal carbonyls.

In other words, by the middle 1960s, computational chemists were using the SCF [20] method to study molecules which contained atoms beyond the first two rows of the periodic table.

The following years were a period of enormous consolidation. Horribly difficult problems could start to be addressed because it was possible to program in FORTRAN, and computers became reliable and more readily available. The convergence of the SCF equations was attacked with success, as it was vital to minimize the number of iterations of this linearized cubic problem. The evaluation of the two-electron four-centre Gaussian integrals was attacked and solved in at least three highly efficient ways [21, 22]. Open- and closed-shell systems were studied using restricted and unrestricted methodologies [23, 24]. The basis function problem was cracked through the introduction of contracted combinations of Gaussian functions [25–27], with standard sets becoming common. Then Pople and co-workers announced their GAUSSIAN program [28], which contained many of these ideas, but which primarily was robust, worked and was freely available to all those who had a Vax computer. By 1970, computational quantum chemistry as we know it today had been born.

Much of the work in standard quantum chemistry over the next 20 years is not directly relevant to us, although it was mathematically brilliant and exceedingly original. The problem at hand was that part of the energy which was missing from Hartree–Fock calculations, namely the electron correlation energy [29]. Although a small contribution, it is nevertheless vitally important in molecular processes. (The correlation energy contribution to the binding of the nitrogen molecules is 100 kcal mol<sup>-1</sup>.) It was believed that the proper approach was to use methods which were related to CI [18] or the linear combination approach. It is, however, important to mention outstanding contributions, such as the multiconfiguration self-consistent field (MCSCF) [30] approach, the Møller–Plesset [25] theory up to fourth order and CC theory [7]. Combinations of these approaches such as multireference double configuration interaction (MRDCI) [31] and complete active space and perturbational treatment (CASPT2) [32] are also widely used. Each of them has the valuable property that there is a straightforward route to improvement. All these methods produce the

highest-quality results, but the downside is that they are all in principle much more expensive than SCF. They are not the way forwards towards large molecular studies. It is, however, important to recognize that this period was also a benchmarking period in which the relative accuracy of different approaches was assessed [33].

There was one important development in the period; Pulay [34] introduced his gradient theory for geometry optimization, ideally suited to the use of Gaussian basis functions. Molecular structures can now be optimized for all methods.

The study of molecules containing transition-metal atoms is a more difficult problem [35], where the chemical bond is weak. Roos [35] highlighted the difficulties of  $\text{Ni}(\text{CO})_4$ , in which the nickel atom is  $d^{10}$ , while in the atom it is  $d^9$ . The correlation effects between the  $d$  electrons and the relativistic contributions cannot be neglected. In *ab initio* quantum chemistry, the MCSCF method is essential to study first-row transition-metal complexes. Roos also referred to the large number of valence electrons; in  $\text{Cr}(\text{CO})_6$ , there are 66 and the correlation energy of all these electrons must be computed. Such a problem is almost impossible using MCSCF techniques, even with today's computers. These three problems (orbital occupancy, relativistic effects and number of participating electrons) exist, often with increasing effect, as one works down the periodic table.

The prototypical molecule for actinide studies is  $\text{UF}_6$ . Early calculations of the one-electron energy levels in 1976 by Koelling *et al.* [36] used the fully relativistic Dirac–Slater method with numerical atomic orbitals. The Slater part means that  $\rho^{4/3}$  is used for exchange and correlation. *Ab initio* SCF and CI calculations using relativistic effective core potentials for uranium were reported in 1979 by Hay *et al.* [37]. This was a major step forwards because the large number of electrons problem was overcome. The orbitals could be examined in detail and the bond length was optimized. Since that time, quantum chemistry methods have become more sophisticated; see for example the fully relativistic four-component Dirac–Hartree–Fock + CI calculations by De Jong and Nieuwpoort [38] for the photoelectron spectrum of  $\text{UF}_6$ . However, the complexity of these sophisticated and accurate methods means that they cannot be applied to larger actinide complexes.

The success of calculations on  $\text{UF}_6$  using the relativistic  $X\alpha$  method (see for example those by Onoe *et al.* [39]) encourages the study of actinide complexes using DFT. If it was 1989 today, we do not think that the MAGIC project would have commenced. Perhaps this would have been because we had not thoroughly read the literature. We were aware of Slater's [15]  $X\alpha$  method of 1954 in which he removed exchange from the SCF equations, replacing it by a term involving  $\rho^{1/3}$ , where  $\rho$  is the electron density. Unfortunately it was multiplied by an empirical constant. Slater said that it worked, it did (or did not) include correlation effects and it came from the uniform electron gas. It was given low attention because it was oversold. Anybody who used it knew that molecules were overbound compared with experiment. We were not familiar with the Hohenberg–Kohn [40] theorems, or the Kohn–Sham [41] construction, or Bright Wilson's [42] incisive understanding. We ought to have been, because our colleagues down the road in physics were using it successfully all the time.

We must make it clear that 'we' refers to 'us', and not all. In particular, Baerends [43] was working with this DFT approach in the early 1970s. He was actually working with hydrogen-like basis functions as well. His group [44] and others [45] were obtaining useful results. In particular, Ziegler *et al.* [46] were producing quality results for transition-metal complexes. We think that the reason that people did not go into DFT earlier was that the molecules were overbound by the theory.

Then came the breakthrough; Becke [9] in his first classic paper showed that the predictions were remarkably improved if the exchange–correlation functional went beyond the local-density approximation (LDA) [47] and included some dependence on  $\nabla\rho$ . His second classic paper [48] told us how to evaluate accurately the matrix elements of these DFT functionals. Becke’s results were impressive; atomization energies were suddenly very accurate; Pople was impressed and introduced Kohn–Sham DFT into GAUSSIAN, and we followed soon after [49].

The enormous attraction of DFT is its cost; in an elementary evaluation it is a SCF method with Hartree–Fock cost. Electron correlation effects are there through the functional, and not through the basis. It is possible to use an orbital model, which all chemists like. Programming it is relatively simple. Not only does it give quality predictions for first- and second-row molecules, but also it works very well for transition metal and actinide complexes and their properties. Many calculations by Dickson and Ziegler [50] using the Amsterdam density functional code (ADF) [51] of Baerend’s group bear this out. Similar calculations by Eichkorn and Ahlrichs [52] using TURBOMOL [53] also support this. A possible reason may be that the band-type structure of these heavier atoms is more amenable to the LDA approximation.

For all these reasons, computational chemistry became a DFT field and, by 1995, the sceptical quantum chemistry community was dragged reluctantly into the DFT arena. DFT calculations were reproducible, which has always been the hallmark of quantum chemistry. Favourite functionals exist, both with (hybrid) and without (generalized gradient approximation (GGA)) some Fock exchange contribution.

Faced with the scientific problems outlined in the introduction, we had decisions to make. We had a specific type of chemical problem to study. All DFT programs in 1995 (with the exception of Baerend’s) were cobbled from a regular quantum chemistry SCF code. There had to be advantages from starting from scratch, which we did. An important initial decision was not to include Fock exchange (this may have been an error), and this had consequences for our evaluation procedures for the Coulomb potential (see section 4). We therefore set about writing a DFT Kohn–Sham code specifically designed to perform calculations on actinide complexes. Before proceeding further, we must discuss relativistic effects (in the next section).

### 3. Relativistic theory

The entire MAGIC project commenced from a visit by Mr A. M. Simper, a research employee of British Nuclear Fuels plc, to N. C. Handy. Adrian Simper expressed an interest in investigating quantum chemistry for actinide complexes. We recognized the immediate problems: the numbers of electrons and the essential relativistic considerations. Adrian then became a graduate student with N. C. Handy to study ‘relativistic calculations on molecules’. Nearly all this section is therefore abstracted from his PhD thesis (1998).

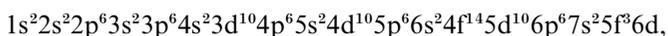
The simple Bohr model of a relativistic atom suggests that the relativistic radius of the uranium 1s orbital is 0.74 of the non-relativistic radius. The immediate knock-on effects are the stabilization of s and p orbitals, and the destabilization of higher-angular-momentum orbitals. In particular the 6s orbital becomes occupied earlier than expected. The atomic radii of lanthanides and actinides are significantly affected by the stabilization of the 6s and 7s orbitals respectively.

In relativistic quantum mechanics, one starts with the four-component Dirac

equation  $h^D\Psi = E\Psi$ . In many-electron theory it is now generally agreed that the best Hamiltonian is constructed from, firstly, the Dirac Hamiltonian  $\Sigma h_i^D$ , secondly, the Coulomb term  $\Sigma e^2/r_{ij}$  and, thirdly, the spin–other orbit interaction of Gaunt and the Breit retardation corrections.

Four-component atomic relativistic codes have existed for some time, in particular the GRASP code due to Grant and co-workers [54], and the code due to Desclaux [55]. The GRASP code is a numerical Dirac–Fock (i.e. SCF) code, with the Breit terms introduced as a perturbation (with the possibility of evaluating quantum electrodynamic terms as well). The Desclaux code is earlier. Four-component relativistic calculations have been and are undertaken. Malli and Pyper [56] used numerical atomic relativistic orbitals in an early study of AuH at the Dirac–Fock and CI level. They showed that relativity shortened the bond by 0.24 Å. Nieuwpoort [35] used a four-component code, originating with the studies of lanthanide compounds. The code MOLFDIR due to Nieuwpoort and co-workers [57] is a Dirac–Fock program for closed- and open-shell molecules, with the possibility of CI on top. Spin–orbit effects are automatically included, and it was suggested that the code is useful as a benchmark for calculations on relatively small molecules. Calculations on PtH,  $\text{EuO}_6^{9-}$  and  $\text{CeF}_8^{3-}$  have been reported. Another four-component code is due to Dyall [58]. For our purposes, such four-component studies do not seem warranted if they can be avoided, primarily because of expense, but also owing to extreme programming difficulties. If four-component studies are envisaged, then the ugly problem of ‘variational collapse’ arises unless the basis set for the small component is specifically derived from the basis set of the large component.

Therefore we looked at two-component models. The simplest, and most appealing if it is accurate enough, is the method of effective core potentials (ECPs). The principle is that we are only interested in the valence electrons which are responsible for the chemical behaviour. For example the complete electronic structure of the uranium atom may be



and it is probably wise to consider that the bulk of the chemistry may be understood in terms of the 7s, 5f, 6p and 6d orbitals. Thus one represents uranium as  $[\text{Pt}]6p^6 7s^2 5f^3 6d$ . The occupancy of these s, f, p and d orbitals will be uncertain in a molecule, but that can become clearer once the platinum core is treated. In MAGIC, we use the method introduced by Kahn, Baybutt and Truhlar (KBT) [59], as refined by Hay and Wadt [60, 61]. We have reprogrammed the ECP equations and integrals (details are given below) but here we simply introduce the concepts.

The essence of the ECP approach as it is now used is contained in the equation for a valence orbital with angular momentum  $l$  for an atom

$$\left( -\frac{1}{2}\nabla^2 - \frac{Z - N_c}{r} + \frac{l(l+1)}{2r^2} + V + U_{\text{ECP}} \right) \chi_l = \varepsilon_l \chi_l. \quad (3.1)$$

$V$  is the Coulomb+exchange+correlation potential and  $U^l$  is a non-local potential which includes the effects of core–valence interaction, core shielding and overcomes the nodal problem (a Phillips–Kleinman potential). The form used by KBT for the total ECP for an atom is given by

$$U_{\text{ECP}} = U_{\text{ECP}}^{l_{\text{max}}} + \sum_{l(m)=0}^{l_{\text{max}}-1} (U_{\text{ECP}}^l) |lm\rangle \langle lm|, \quad (3.2)$$

$$\frac{N_c}{r} + U_{\text{ECP}}^{l_{\text{max}}} = \sum_k d_k r^{n_k} \exp(-\alpha_k r^2), \quad (3.3)$$

$$U_{\text{ECP}}^l = \sum_t c_t r^{n_t} \exp(-\beta_t r^2). \quad (3.4)$$

Here  $l_{\text{max}}$  is the maximum angular momentum in the core.

The extension to include the dominant relativistic terms (mass–velocity, spin–orbit and Darwin) is straightforward because they are one-electron operators; one simply performs two-component calculations including these operators. The ECP parameters which we use were determined from post-Hartree–Fock atomic two-component relativistic calculations (i.e. they were determined from CI calculations and not DFT calculations). This immediately introduces the question of whether it is safe to combine these ECP parameters with DFT in the valence space; we merely assume that this does not introduce substantial errors.

Of course the ultimate test is the comparison with all electron calculations. Both KBT and Hay and Wadt introduced devices to make the valence orbitals resemble two-component Hartree–Fock orbitals, which were smooth in the core region and appeared good in the tail regions. However, we have found that agreement between various forms of ECP and the corresponding all-electron DFT calculation is generally good and certainly within the ‘chemical accuracy’ bounds of MAGIC. Bond energies have millihartree agreement, bond lengths agree to hundredths of a bohr, and angles to tenths of a radian. Such comparisons, however, have to be treated with care because of the prescribed basis sets which are used in ECP calculations.

The major cost of an ECP calculation is the evaluation of

$$\langle \eta(C) | U_{\text{ECP}}(A) | \eta(B) \rangle, \quad (3.5)$$

where  $U_{\text{ECP}}(A)$  is the ECP potential defined earlier on centre A, and  $\eta(B)$  and  $\eta(C)$  are any Cartesian Gaussians on centres B and C respectively. We first examined the ECP code as written some years ago by Hay and Wadt; we found it slow and not sufficiently flexible for us, and we therefore decided to write our own algorithms for these matrix elements. Details of this work due to A. M. Simper and C.-K. Skylaris are given in the next section.

MAGIC also has the facility to perform more sophisticated two-component relativistic calculations, which introduce to some extent the effects of the small components.

The first approach is commonly known as the CPD transformation. Much of the original work involving renormalization of the large component was due to van Lenthe *et al.* [62]. The key lies in the relation

$$\psi_s = \frac{1}{2mc} \left( 1 + \frac{E-V}{2mc^2} \right)^{-1} \sigma \cdot \mathbf{p} \psi_L, \quad (3.6)$$

which allows the Dirac equation to be written as

$$\left[ V + \frac{1}{2m} \sigma \cdot \mathbf{p} \left( 1 + \frac{E-V}{2mc^2} \right)^{-1} \sigma \cdot \mathbf{p} \right] \psi_L = E \psi_L. \quad (3.7)$$

Next the inverse operator is rewritten through

$$\frac{1}{2} \left( 1 + \frac{E - V}{2mc^2} \right)^{-1} = \frac{mc^2}{2mc^2 - V} \left( 1 + \frac{E}{2mc^2 - V} \right)^{-1} \quad (3.8)$$

and then one expands  $(1 + E/(2mc^2 - V))^{-1}$ . This then yields the zeroth-order regular approximation Hamiltonian  $H_0^{\text{CPD}}$ :

$$H_0^{\text{CPD}} = V + \sigma \cdot \mathbf{p} \frac{c^2}{2mc^2 - V} \sigma \cdot \mathbf{p}. \quad (3.9)$$

An expansion of  $H_0^{\text{CPD}}$  then shows that it contains the ordinary Newtonian terms ( $p^2/2m$  and terms in  $\mathbf{A}$  and  $A^2$ ), the Darwin term ( $(\hbar^2/8m^2c^2) \nabla^2 V$ ), the spin-orbit term ( $(1/4m^2c^2) \sigma \cdot (\nabla V \times \mathbf{p})$ ) and the magnetic spin interaction ( $-(e\hbar/2mc) \sigma \cdot \nabla \times \mathbf{A}$ ).

The implementation of CPD into a DFT code yields the following orbital equation, assuming that the energy expression is the usual DFT expression of Kohn–Sham theory, with  $T$  replaced by  $T^{\text{CPD}}$ , and after the neglect of a higher-order term:

$$(T^{\text{CPD}} + v_{\text{ext}} + v_{\text{J}} + v_{\text{xc}} - \varepsilon_i) \psi_i = 0, \quad (3.10)$$

where

$$T^{\text{CPD}} = \sigma \cdot \mathbf{p} \frac{c^2}{2mc^2 - V} \sigma \cdot \mathbf{p}. \quad (3.11)$$

If we then introduce the usual space–spin basis  $(A_i \alpha, B_i \beta)$ , then the matrix element of  $T^{\text{CPD}}$  between two such basis functions is

$$\begin{aligned} T_{ij}^{\text{CPD}} = \int d\mathbf{r} [ & A_i^x f A_j^x + A_i^y f A_j^y + A_i^z f A_j^z + i(A_i^x f A_j^y - A_i^y f A_j^x) \\ & + B_i^x f B_j^x + B_i^y f B_j^y + B_i^z f B_j^z + i(B_i^x f B_j^y - B_i^y f B_j^x) \\ & + A_i^z f B_j^x + B_i^x f A_j^z - A_i^x f B_j^z - B_i^z f A_j^x \\ & + i(A_i^y f B_j^z + B_i^y f A_j^z - A_i^z f B_j^y - B_i^z f A_j^y), \end{aligned} \quad (3.12)$$

where  $f(\mathbf{r}) = c^2/[2c^2 - V(\mathbf{r})]$ , and the superscripts denote the first derivatives of the Gaussian basis functions  $(A_i, B_i)$ .

The CPD method was first implemented in the ADF code of Baerend’s group. The difficulty with the approach is the numerical evaluation of the full potential  $V$  at a numerical integration grid point  $\mathbf{r}$ . There is never any problem with the evaluation of the external potential or the exchange–correlation potential, but the Coulomb potential does cause difficulties. In the ADF code the density is represented in terms of a fitted Slater-type orbital (STO) basis, for which the potential is also trivial. In our case the problem is difficult, we proceeded through the evaluation of Gaussian nuclear attraction integrals at each grid point, which is costly. Furthermore we found it was necessary to use more quadrature points to evaluate this matrix element reliably. Therefore this CPD code using a Gaussian basis is only recommended for trial investigations.

The other approach which is available within MAGIC is the DK method. The approach here is to find a unitary transformation  $\tilde{H} = UH U^\dagger$ , so that  $\tilde{H}$  does not couple the large and small components. The important references are the papers by Foldy and Wouthysen [63], Douglas and Kroll [2], Hess [64] and Knappe and Rosch [65].

Here we write  $U = U_0 U_1$ , where  $U_0$  is the Foldy–Wouthysen transformation,

which is an exact decoupling in the absence of an external field. This gives the transformed Dirac Hamiltonian  $h_1^D$ :

$$h_1^D = \beta E_p + A(V + RVR)A + \beta A(RV - VR)A, \quad (3.13)$$

where

$$A = \left( \frac{E_p + mc^2}{2E_p} \right)^{1/2}, \quad (3.14)$$

$$R = \frac{c\boldsymbol{\alpha} \cdot \mathbf{p}}{E_p + mc^2}, \quad (3.15)$$

$$E_p = (c^2 p^2 + m^2 c^4)^{1/2}. \quad (3.16)$$

The decoupling is exact in the absence of an external field.

DK then introduced

$$U_1 = (1 + W^2)^{1/2} + W. \quad (3.17)$$

For a  $W$ , whose kernel is given in the momentum representation by

$$W(p, \bar{p}) = \frac{ARV - VRA}{E_p(p) - E_p(\bar{p})}, \quad (3.18)$$

one obtains the two-component one-electron DK Hamiltonian

$$h_2^{\text{DK}} = E_p + A(V + RVR)A - \left( \frac{1}{2} [W^2, E_p]_+ + WE_p W \right). \quad (3.19)$$

This is the one-electron operator implemented in MAGIC. It exactly decouples the small and large components through second order. An analysis of terms through  $c^{-2}$  gives

$$E_p = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2}, \quad (3.20)$$

$$AVA = V - \frac{1}{8m^2 c^2} [p^2, V], \quad (3.21)$$

$$ARVRA = -\frac{\hbar}{4m^2 c^2} \boldsymbol{\sigma} \cdot (\nabla \mathbf{V}) \times \mathbf{p} + \frac{1}{4m^2 c^2} \{ \mathbf{p} \} \mathbf{V} \{ \cdot \mathbf{p} \}. \quad (3.22)$$

The Newtonian terms are there, the Darwin term is there, as is the spin-orbit interaction. The unbounded mass-velocity term is also present and is not cancelled by the  $W$  terms.

Subtracting  $mc^2$  yields the two-component DK DFT operator

$$F^{\text{DK}} = T^{\text{DK}} + v_J + v_{\text{xc}}, \quad (3.23)$$

$$T^{\text{DK}} = E_p - mc^2 + AVA + ARVRA - WE_p W - \frac{1}{2} (W^2 E_p + E_p W^2). \quad (3.24)$$

To work in MAGIC we now introduce a Gaussian basis set as usual. We must transform to momentum space by diagonalization of the basis function representation of the kinetic energy. Since  $p$  is diagonal in the momentum basis, it follows that the operators  $E_p$ ,  $A$  and  $R$  have a diagonal representation as well. The difficulty comes in the matrix representation of operator products owing to the incomplete basis. Hess has shown that we must proceed through

$$C_{ij} = (AB)_{ij} = \sum_k A_{ik} B_{kj}. \quad (3.25)$$

Indeed this is so critical that we introduce the full uncontracted basis in the

completeness relation. Further algebra gives the following representations for the remaining terms:

$$ARVRA = \hbar^2 A' V_{\mu\mu} A' + i\hbar^2 \varepsilon_{\mu\nu\omega} \sigma_\omega A' V_{\mu\nu} A', \quad (3.26)$$

$$A' = \frac{cA}{c^2 + E_p} \quad (3.27)$$

$$V_{\mu\nu} = \langle \nabla_\mu \xi_i | V | \nabla_\nu \xi_j \rangle \quad (3.28)$$

$$W^2 = (ARVRA)(AVA) - (AVA)(R^2)(AVA) \\ - (ARVRA)(R^2)(ARVRA) + (AVA)(ARVRA), \quad (3.29)$$

$$WE_p W = (ARVRA)E_p(AVA) + (AVA)E_p(ARVRA) \\ - (AVA)R^2E_p(AVA) - (ARVRA)E_pR^2(ARVRA). \quad (3.30)$$

This completes the description of how this Hamiltonian was programmed within MAGIC.

As written, this DK code had substantial memory requirements because of the necessity to use the uncontracted basis. To overcome this cost we introduced a ‘two-centre’ approximation [66]. This works as follows. Submatrices on two specific centres were extracted, and then the DK transformation performed using all the primitives on those two centres. The elements are then pushed back. The two-centre approximation greatly reduces the memory requirements, while retaining the millihartree accuracy requirement. In conclusion to this section, the inclusion of relativistic effects into MAGIC was the PhD research topic of A. M. Simper. The ECP code forms the straightforward production method; the CPD and DK methods are available, but only for more detailed research purposes.

## 4. One- and two-electron integral evaluation

### 4.1. Introduction

All one-electron integrals of MAGIC are calculated before a SCF calculation and stored in the archive. From there, they are retrieved whenever a module needs them.

The number of basis functions necessary to study the size of systems for which MAGIC is intended results in a prohibitively large number of two-electron integrals. It is impossible to keep all these in memory or even to store them on disk. MAGIC is therefore a direct SCF program and it computes the two-electron integrals from the beginning at every SCF iteration, based on the principles of direct SCF pioneered by Almlöf *et al.* [67] and later elaborated by Häser and Ahlrichs [68]. The neglect of integrals with zero value makes the scaling of the computational cost with the size of the system slightly higher than quadratic.

The two-electron integral subroutines are brand new and implementationally not related to any of the previous two-electron integral evaluation packages. The theory that we implemented to generate the two-electron integrals is that of the quadrature and recursions of Rys and co-workers [69–71] with subsequent refinements such as the reduced multiplication scheme [72] and the use of the transfer equations at the contracted stage [73].

### 4.2. Coulomb energy evaluation in MAGIC

The direct scheme of MAGIC can calculate two-electron integrals which are used in the evaluation of the Coulomb operator matrix elements of the Kohn–Sham matrix. In some ongoing calculations, they are also used in the exchange operator matrix

elements of the Kohn–Sham matrix in calculations where hybrid functionals are used or for traditional Hartree–Fock calculations.

In DFT calculations that employ functionals with only local exchange the two-electron repulsion integrals contribute only to the Coulomb part of the Kohn–Sham matrix and the corresponding expression for the energy. The Coulomb operator matrix elements  $F_{ij}^J$  can be written in terms of the electronic density  $\rho$  and two basis functions  $\phi_i$  and  $\phi_j$  as a two-electron integral:  $(\phi_i \phi_j | \rho)$ . A very successful approximation which speeds up considerably the calculation is the use of an auxiliary basis set to expand (fit) the density. This fitted density  $\hat{\rho}$  is then used in the evaluation of the Coulomb part of the Kohn–Sham matrix, in place of the ‘true’ density  $\rho$ . As a result, only three-index two-electron integrals are required. There are inherently fewer three-index integrals than four-index integrals and their calculation requires less computational effort anyway. Therefore such an approximation is significantly faster than the conventional four-index two-electron integral approach.

The auxiliary basis density fit method was first developed by Baerends *et al.* [43] and was called the ‘discrete variational method’. Each contribution to the density due to every set of basis functions on a pair of atoms was approximated (fitted) as a linear combination of auxiliary functions based on the same pair of atoms. It was therefore a local fitting procedure, that is it fitted separately each diatomic contribution to the density. Also, in its original form, it involved the evaluation of three-centre overlap integrals and only a two-dimensional matrix of two-electron integrals (two-index) between pairs of basis functions. This fitting scheme was based on the minimization of the mean square deviation between the true and the fitted density.

MAGIC takes advantage of auxiliary basis density fit methods for the significant computational savings that they yield are necessary for quick calculations on the systems that we are aiming for.

The density fitting procedures implemented in MAGIC are based on the improvements of Dunlap *et al.* [74] and Ahlrichs and co-workers [75], which are claimed to yield a more accurate fit. They are based on the minimization of the mean square of the electric field due to the true and the fitted density. This results in the evaluation of three-centre two-electron integrals. Two options for density fitting are available.

- (1) The density  $\rho(\mathbf{r})$  is fitted as a whole according to the following formula :

$$\rho(\mathbf{r}) \approx \hat{\rho}(\mathbf{r}) = \sum_{t=1}^{N_{\text{AUX}}} q_t f_t(\mathbf{r}),$$

where  $q_t$  are the expansion coefficients or charges [76, 77] and  $\hat{\rho}(\mathbf{r})$  represents the fitted density. The elements of the Coulomb contribution to the Kohn–Sham matrix are calculated in two stages. First, the charges are calculated:

$$q_s = \sum_{t=1}^{N_{\text{AUX}}} \sum_{i,j=1}^{N_{\text{BF}}} (V^{-1})_{st} (f_t | \phi_i \phi_j) D_{ji},$$

where  $N_{\text{BF}}$  is the number of basis functions,  $N_{\text{AUX}}$  is the number of auxiliary functions,  $D_{ij}$  is the density matrix and  $(V^{-1})_{st}$  is the inverse of a two-dimensional matrix containing two-electron integrals between the auxiliary

functions. Then, the actual elements of the Coulomb Kohn–Sham matrix are calculated from

$$F_{ij}^J = \sum_{t=1}^{N_{\text{AUX}}} (\phi_i \phi_j | f_t) q_t.$$

We call this the global fitting procedure and it is the preferred way of fitting densities in most DFT programs [78] which use this approximation for the Coulomb part of the energy. It has proved rather accurate for standard calculations and a variety of auxiliary basis sets have been developed by various groups [75, 79, 80]. Furthermore, MAGIC offers the possibility of including auxiliary basis functions centred on any (user-defined) point along the distance between an atom pair or even on arbitrary points in space, should the need for this arise.

- (2) The diatomic density  $\rho_{\text{AB}}(\mathbf{r}) = \sum_{i,j} D_{ij}^{\text{AB}} \phi_i^{\text{AB}}(\mathbf{r}) \phi_j^{\text{AB}}(\mathbf{r})$  due to every pair of atoms A and B is fitted to auxiliary functions centred on these atoms only, resulting in diatomic fitted densities  $\tilde{\rho}_{\text{AB}}(\mathbf{r})$  whose sum is the total fitted density. This scheme is even faster since it requires the consideration of functions only on pairs of atoms. However, it is less accurate since by definition only auxiliary functions on A and B are used to represent each diatomic density  $\rho_{\text{AB}}$ . We call this the local or diatomic fitting procedure. An added difficulty of the local fit is that, currently, there are no auxiliary basis sets available specifically designed for this purpose.

It is worth mentioning that all the integral subroutines of MAGIC, consistent with our programming philosophy, do not involve any limitations on the size of the system being studied and the computational resources that they can occupy. This also implies that there is no limit on the number of basis functions that an atom can have, on their angular momentum or on the number of primitive Gaussians per contraction. Recursions are programmed in full. For low angular momenta, explicit expansions are used for improved computational speed. Such requirements, although trivial, are not taken for granted in some standard quantum chemistry packages.

A statistical analysis of the density fit at the end of the calculation can be performed to check whether the accuracy of the fit is satisfactory and its influence on the result. This, together with a detailed comparison of the above-mentioned three ways to evaluate the Coulomb part of the Kohn–Sham matrix for a variety of basis sets and molecules will be described in a subsequent publication.

### 4.3. Gradient and geometry optimization

MAGIC can optimize geometries through an implementation of a geometry optimizer based on the use of analytic gradients of the energy and an approximation to the Hessian by the Broyden–Fletcher–Goldfarb–Shanno (BFGS) update formula [81, 82]. Such quasi-Newtonian methods have been shown to be rather successful and avoid the high computational cost of directly calculating the Hessian [83, 84]. According to the BFGS formula the inverse Hessian at a specific molecular geometry ( $n$ th step of the geometry optimization) is given by the following expression:

$$\mathbf{G}_n = \left( \mathbf{1} - \frac{\mathbf{q}_n \cdot \mathbf{d}_n^\dagger}{\mathbf{q}_n^\dagger \cdot \mathbf{d}_n} \right) \mathbf{G}_{n-1} \left( \mathbf{1} - \frac{\mathbf{q}_n \cdot \mathbf{d}_n^\dagger}{\mathbf{q}_n^\dagger \cdot \mathbf{d}_n} \right)^\dagger + \frac{\mathbf{q}_n \cdot \mathbf{q}_n^\dagger}{\mathbf{q}_n^\dagger \cdot \mathbf{d}_n}, \quad (4.1)$$

where the column vector  $\mathbf{q}_n = \mathbf{X}_n - \mathbf{X}_{n-1}$  is the difference between the molecular geometry at step  $n$  and at the previous step. In a similar fashion,  $\mathbf{d}_n = \mathbf{g}_n - \mathbf{g}_{n-1}$  contains the difference between the two consecutive gradients.  $\mathbf{1}$  is the unit matrix. As the number of geometry optimization steps increases, the approximation to the inverse Hessian given by equation (4.1) becomes better. Because of the approximate inverse Hessian and the fact that the potential energy surface is not simply a quadratic function of the coordinates, a line search has to be performed and various line search schemes can be used. However, the gain in optimizer steps that a line search yields can be outweighed by the extra point energy evaluations that it requires. In addition, there seems to be no line search scheme which is efficient and robust enough for all types of molecule and levels of theory. We therefore use directly the quasi-Newtonian step vector scaled by a factor less than or equal to unity. The density at the previous geometry is used as a starting density for an SCF calculation during a geometry optimization.

Analytical gradients for SCF functions are essential for geometry optimizations and the formulae for a variety of *ab initio* methods are readily available [85]. MAGIC uses the gradient of the DFT energy calculated using the global density fitting scheme for the Coulomb energy. The expression for the gradient is the same as in the four-index case but with the Coulomb part of the gradient

$$\frac{1}{2} \mathbf{D}^\dagger \frac{\partial \mathbf{H}}{\partial R_{A\gamma}} \mathbf{D} \quad (4.2)$$

replaced by

$$\frac{\partial \Gamma^\dagger}{\partial R_{A\gamma}} \mathbf{V}^{-1} \Gamma - \frac{1}{2} \Gamma^\dagger \mathbf{V}^{-1} \frac{\partial \mathbf{V}}{\partial R_{A\gamma}} \mathbf{V}^{-1} \Gamma, \quad (4.3)$$

where  $\mathbf{H}$  is the four-index two-electron supermatrix,  $\Gamma$  is the three-index two-electron supermatrix and  $R_{A\gamma}$  is a Cartesian coordinate of centre A ( $\gamma = x, y, z$ ). A detailed derivation of the above formalism including extensions for second derivatives has been published by Komornicki and Fitzgerald [86].

Calculation of the gradient requires the use of first derivatives with respect to atomic coordinates of the one- and two-electron integrals that contribute to the energy. The translational invariance principle is employed to save some computational effort [87, 88]. Some attention is due to the evaluation of the derivatives of the exchange–correlation potential matrix elements. These integrals are evaluated by three-dimensional molecular quadrature and errors in the gradient can result with small quadrature grids. These errors disappear in the limit of an infinite grid or if consistency is preserved by taking account of the derivatives of the grid with respect to atomic coordinates as some workers have stated [89–91]. In MAGIC we use large enough grids that lead to negligible errors in the gradient. We prefer such an approach to the computational complexity of grid derivatives because it leads to overall more accurate exchange–correlation energies. The extra overhead due to the larger grid is very small owing to the neglect of zero contributions.

#### 4.4. *Effective core potentials*

The use of ECPs is a necessary approximation in calculations of heavy-element-containing large molecules. This is because most molecules of chemical interest usually include more than ten atoms. For molecules of such size all-electron two- and four-component methods have too high a computational cost for currently available

computer resources, which renders them inefficient for routine calculations. ECPs allow for the incorporation of the most important relativistic effects in the same single determinant framework of non-relativistic Kohn–Sham calculations. In addition, they are constructed in such a way as to yield orbitals with no nodes in the core region, a consequence of which is the use of a smaller (valence only) basis set. These two features of ECPs lead to increased computational speed while maintaining sufficient accuracy.

The derivation of ECPs according to KBT [59] has proved particularly successful and popular in molecular calculations. A large number of researchers have derived ECP parameters and matching valence basis sets for the KBT scheme for almost all the atoms of the periodic table and with various degrees of sophistication in their derivation. As a small part of what is available we mention the ECPs derived by Hay and Wadt [60, 61] and Wadt and Hay [92] and the newer ECPs by the Stuttgart group [93–95]. The latter contain two different ECPs for each element, one which has been derived using standard non-relativistic theory and one which has been derived by taking into consideration relativistic effects. It is then possible to use the two kinds of ECP to run two sets of calculations and to obtain an estimate of the changes that the consideration of relativity causes on a molecule.

The KBT-type ECPs are conveniently expressed as linear combinations of Gaussian functions (see equations (3.2)–(3.4)). In all ECPs derived to date the powers  $n_{kL}$  and  $n_{kl}$  are restricted to the values 0,  $-1$  and  $-2$ . In MAGIC, the ECP parameters are kept in a library file just like basis sets and the addition of new ECPs is a trivial matter.

All the computational effort of using ECPs lies in the calculation of the integrals of the one ECP operator with the basis functions. Once those are calculated, they can be treated as the rest of the one-electron integrals and no more computational effort is required. A few methods and corresponding programs for evaluating these matrix elements have been developed over the years [59, 96–98].

MAGIC has built in from the beginning the ability to use the KBT form of ECPs in all the types of calculations that it supports. Their implementation is described in the following section.

#### 4.5. *Effective core potential integral evaluation*

As with all of MAGIC, the ECP integral code has been written from the beginning. The KBT ECP operator matrix elements are expressed as sums of two kinds of one-electron integral:

$$\chi_{AC} = \int \phi_A r^{n_{kL}} \exp(-\zeta_{kL} r^2) \phi_C d\tau \quad (4.4)$$

and

$$\gamma_{AC} = \int_0^\infty \langle \phi_A | lm; B \rangle (r) r^{n_{kL}+2} \exp(-\zeta_{kL} r^2) \langle \phi_C | lm; B \rangle (r) dr, \quad (4.5)$$

where  $\phi_A$  and  $\phi_C$  are primitive Cartesian Gaussian functions on centres A and C respectively.

We evaluate the  $\chi_{AC}$  integral according to the confluent hypergeometric formula presented by McMurchie and Davidson [96]. For the evaluation of the  $\gamma_{AC}$  integral we have implemented a variant of the McMurchie–Davidson method [99]. The original implementation proved too slow for the types of molecule that we wish to study. We therefore derived a new, more efficient way of evaluating this particular integral. It is a mixed numerical–analytical integration technique. It exploits the fact that the Gaussian functions in  $\gamma_{AC}$  are independent of each other as far as angular integration

is concerned and the high efficiency of the Log3 radial quadrature scheme [100] for molecular integrals.

The angular integrals  $\langle \phi_A | lm; B \rangle(r)$  are calculated by analytical integration at every radial point of the Log3 quadrature. Then they are used to calculate the  $\gamma_{AC}$  integral as a whole:

$$\gamma_{AC} = \sum_{i=1}^{n_r} \langle \phi_A | lm; B \rangle(r_i) \langle \phi_C | lm; B \rangle(r_i) r_i^{n_{kl}} \exp(-\zeta_{kl} r_i^2) w_i, \quad (4.6)$$

where  $n_r$  is the number of radial quadrature points, and  $r_i$  and  $w_i$  are the corresponding points and weights respectively. The accuracy of the numerical part of the integration is controlled by increasing the number of points in stages until a predefined precision ( $10^{-10}$  in our case) is achieved. It can be extended to scale linearly and, as the rest of MAGIC, it has no limitations on the number of basis functions, angular momentum and size of system. Calculations on actinide complexes with large ligands and metal clusters with many ECP centres are well within the reach of the method. A detailed description of the method has been published [10].

### 5. The self-consistent field procedure

The Fock operator for a Kohn–Sham procedure leads to a complicated high-dimensionality nonlinear equation to be solved. Solution of such an equation allows us to represent the orbitals for the system within our model. As an analytic solution is not available, and unlikely ever to be so, an iterative scheme is used. However, it is not clear that an iterative scheme will always be able to find a solution.

The problems of finding such solutions have been well documented in the literature, particularly in the cases of open-shell molecules [102] and those described by multiconfiguration methods [30]. A number of solutions have been proposed, most of which have found success in solving a particular type of convergence difficulty.

In addressing convergence difficulties, two approaches may be considered. In analogy with observations in chaos theory, convergence behaviour may be changed by changing the initial conditions, or by changing the form of the Fock operator. Examples of the former include changing the initial guess orbitals, the atomic basis sets, the geometry and the occupation of the initial orbitals by altering the spin multiplicity. The way in which the convergence behaviour depends upon these parameters is clearly very complicated. In the case of the guess orbitals, for example, the general rule is that, the ‘better’ the initial guess, the faster the convergence. However, this assumes that one knows what ‘better’ is and in the limit actually assumes knowledge of the solution. Although this may be possible by analogy with similar systems, which one has previously analysed, an absence of such comparisons may lead to inaccurate assumptions. The other variables mentioned relate to the detailed mathematical description of the system. A direct connection between these and convergence behaviour has not been established. Even if it were, it is not clear that this could be used to improve such behaviour. One is often also obliged to use certain starting parameters, such as using a geometry obtained from experiment.

Another commonly used technique is to converge for a system related to the system under investigation and then to use its density as a starting point for the true system. For example, where it is not possible to converge the system with a stretched bond directly, it may be possible to converge for a shorter bond length. The density from this calculation would then be used for the system with a slightly stretched bond. This process would be repeated until the desired bond length has been attained.

Much attention has been given to methods involving changing the form of the Fock operator. One such method is the use of level shifting proposed by Saunders and Hillier [103]. The idea is that convergence behaviour may be improved by applying a shift to the virtual orbital eigenvalues. This does not affect the final energy. One case in which this will clearly help is in making degenerate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) non-degenerate, although it appears to be of considerable assistance in other cases. The value of the level shift has been examined. We adopt the simplest approach which is to shift all virtual eigenvalues by the same fixed amount. The value of the shift is typically four, although some systems require a much larger value. This technique forms an important part of the basic MAGIC model.

Scaling has been widely used to improve convergence. For example it is possible at any given iteration to scale the nonlinear part of the Fock operator such that the total energy is minimized. One then proceeds to the next iteration, making use of this revised Fock operator. Such schemes have been examined by Seeger and Pople [104].

Direct inversion of the iterative subspace (DIIS) was first introduced by Pulay [105] to accelerate the self-consistent procedure to a solution. One simply forms a linear combination of previous Fock matrices at any given iteration. The coefficients within this combination are calculated on the basis of an error vector, which is any property of the system which becomes zero at convergence. This is typically chosen to be the vector given by  $FDS - SDF$ . Clearly such a transformation involves a change in the form of the Fock operator and, as such, is often used to help to find a solution. Numerical difficulties may arise in the DIIS procedure from the use of error vectors which are becoming very small towards convergence. The C2-DIIS method of Sellers [106] is used within MAGIC to overcome some of these. It basically involves the diagonalization of a matrix and an appropriate selection of eigenvector for the expansion coefficients.

One may consider methods which do not involve diagonalization of the Fock matrix. These methods will obviously avoid any problems arising from degenerate eigenvalues of the Fock matrix. The large fluctuations in density are also avoided.

An example of this technique is direct energy minimization (DEM) [107]. One begins from the observation that the total energy of a molecule is minimized by rotating the virtual orbitals into the occupied orbitals. Therefore, if the rotation matrix were known, it would be possible to rotate the occupied orbitals directly to give the lowest possible energy. However, the rotation matrix is not normally known. We suppose that the change in the rotation matrix as we move about the orbital surface is governed by forces which obey Newton's law. If we can calculate the forces, we can integrate to give simple equations of motion for the rotation matrix elements. It happens that it is possible to evaluate the forces and indeed they are proportional to the MO Fock matrix. This leads to simple equations of motion which describe the evolution of the rotation matrix. In this form we simply move about the orbital surface. However, the scheme is easily adjusted to become a steepest-descent procedure which finds the lowest possible energy. When this is true, the rotation matrix is clearly zero. One satisfying aspect of the scheme is that the convergence criterion often is that the MO Fock matrix elements become zero. Once the new rotation matrix has been found, a Levy [108] transformation of the occupied orbitals is performed. Although a finite number of terms in the exponential expansion are used, problems due to orbital orthogonality do not normally arise.

An alternative procedure is the conjugate gradient density matrix search [109].

Here it is the density matrix which is adjusted, subject to maintaining its idempotency ( $\mathbf{D}^2 = \mathbf{D}$ ). This latter restriction is imposed by the application of a purification transformation, defining a new density matrix as  $3\mathbf{D}^2 - 2\mathbf{D}^3$  [110]. The scheme involves the minimization of a function of the density, which is typically  $F\mathbf{D}$ . The conjugate gradient technique is used to accomplish this.

Both of these methods are more robust in finding a solution than standard diagonalization techniques. However, their disadvantage is that they are slow.

It is important to consider further details of the self-consistent procedure. The first is the way in which convergence is checked for. The simplest way is to look at the absolute difference in total energy in successive iterations and indicate convergence when this drops below a certain threshold. Computational issues limit how strictly this threshold may be set. Such a scheme leads to a significantly less well converged electron density. Further use of this density, in the calculation of molecular properties, may therefore lead to unsatisfactory results. Accuracy is therefore improved by converging on the density. This may be accomplished by checking the absolute difference in the density matrix between successive iterations or, even more strictly, the root mean square deviation in this matrix. This is the standard within the MAGIC model. When DIIS is used, it is more elegant to check the magnitude of the error vector, which is done. In the DEM procedure, the obvious check is on the maximum absolute element of the MO Fock matrix.

A second important point concerns the nature of the solution. When such a solution is obtained, it is merely a stationary point and, as such, may be a minimum, maximum or point of inflection. To verify that a minimum has indeed been located, it is necessary to perform a 'stability analysis' [111]. This involves the calculation of second-derivative properties and work is under way to include this in MAGIC. However, if the solution is not a minimum, this does not tell one how to find the minimum, or indeed whether it exists.

There are a number of problems with finding solutions to nonlinear equations which these methods attempt to address. The simplest is perhaps that due to density fluctuations which occurs, for example, in the restricted treatment of the hydrogen molecule with an extended bond length. Two solutions to the problem are possible, namely  $\text{H}^+ + \text{H}^-$  or  $\text{H}^- + \text{H}^+$ . One therefore finds an oscillation in the iterative scheme between these two possibilities. To find a solution, one uses either an unrestricted model or the level shift technique, which appears to find the same solution. Another straightforward difficulty is in the treatment of degenerate eigenvalues of the Fock matrix. In this case a swapping of eigenvectors takes place in successive iterations, leading to artificial differences in the density matrices. This is most easily solved by avoiding the use of diagonalization. When one considers the actinide elements, their electronic structure makes location of solutions difficult. This is partly because of the small energy difference between many of the valence orbitals. Density fluctuations typically occur, with electrons moving easily between different orbitals in successive iterations. It is interesting that we usually observe an oscillation between only two possible configurations.

A typical MAGIC calculation involves a combination of techniques. It is found that the initial use of a level shift or DEM helps to stabilize the iterative scheme. The value of the level shift may be either 4.0 or 20.0. Where a value of 20.0 has been used, this is normally reduced after about 15–20 iterations to a value of 4.0. It is then usually found necessary to keep the level shift applied to final convergence. This often proves to be a very slow procedure. Where DIIS can be used, this is preferred.

The convergence of the SCF iterations remains an ongoing research topic. At present we are examining a ‘non-integer’ occupancy scheme if there is a band-type structure to the orbital energies. This is similar to a MCSCF approach, but in the DFT formalism.

## 6. Density functional theory

Our opening policy was not to include the possibility of including any Fock (exact) exchange in the energy expression, although we are now questioning this decision. Therefore in the MAGIC program we use GGA functionals, namely those for which the exchange–correlation energy expression is

$$E_{xc}[\rho] = \int f_{xc}(\rho_\alpha, \rho_\beta, \zeta_{\alpha\alpha}, \zeta_{\alpha\beta}, \zeta_{\beta\beta}) \mathbf{r}. \quad (6.1)$$

In this expression  $\rho_\sigma, \sigma = \alpha, \beta$  are the spin densities, and  $\zeta_{\sigma\sigma'} = \nabla \rho_\sigma \cdot \nabla \rho_{\sigma'}$ . The program is written in terms of spin densities.

In the program the exchange–correlation potential  $v_{xc}(\mathbf{r})$  is not specifically evaluated in the Kohn–Sham part, because an integration by parts removes the necessity for the evaluation of second derivatives of  $f_{xc}$ . However,  $v_{xc}(\mathbf{r})$  is required for the evaluation of the energy gradient, necessary for any geometry optimization. Such subroutines have been independently written and checked. The functionals in use in MAGIC are LDA [112, 113] and BLYP [9, 10].

The latest version of MAGIC involves the evaluation of the DFT parts in  $O(N)$  cost, that is the cost goes up linearly with increasing size of the molecule. All the DFT matrix elements and exchange–correlation energies must be evaluated by quadrature, which means the generation of a quadrature grid and associated weights. The Becke procedure is used to partition molecular space into atom-centred Voronoi polyhedra, within which a spherical polar grid is generated. The number of such grids is equal to the number of atoms. For each grid point, a list of those basis functions which are significant (less than  $10^{-9}$ ) is generated. All loops inside over basis functions will only involve this list. The code is therefore  $O(N)$  cost.

The specifics of the grid now follow. For the radial grid we use the recipe of Mura and Knowles [100], for which the specific parameters for our atoms are  $\alpha = 5$  or  $7$ , depending on the atomic number. For the angular grid we always use the two-dimensional Lebedev set, using 110, 302, 590 or 974 points [114]. The code makes its automatic selection according to a specific data set instruction. We have found no evidence of instability with these choices, and we expect that the Kohn–Sham energies which we calculate to be accurate to  $0.001E_h$ .

The DFT part of the code is efficiently written, and in no way is a dominant part of the calculations. New functionals may trivially be added as appropriate. However, it must be stressed that the use of DFT to study actinides is definitely a semiempirical approach which has not yet been adequately validated.

## 7. Solvent effects

As mentioned previously, a large part of the chemistry that is of interest to British Nuclear Fuels plc takes place in the liquid phase. This prompts us to extend the gas-phase computations to incorporate the effects of such an environment. One of the current strategies for the inclusion of solvent effects is the use of a continuum solvent model. The solute, or system of chemical interest, is housed inside a cavity in an infinite dielectric continuum which assimilates the bulk liquid. Such models effectively involve the addition of a solvent term into the quantum-chemical Hamiltonian. Models such as the polarizable continuum model of Tomasi and co-workers [115] and continuum

solvation model (COSMO) [116] are two examples. The formalism of these models explicitly uses the induced charge density on the cavity surface as a variable in the model. The model that we have used is based on the reaction field concept of Onsager [117] and it uses the formalism of the self-consistent reaction field method, introduced by Rivail and Rinaldi [118]. This model seems more elegant as it only involves the use of the size and shape of the cavity, the dielectric constant of the continuum and the properties of the solute inside the cavity to calculate the electrostatic contribution to the solvation free energy, thus bypassing the direct use of the surface charge density. We give a brief outline below.

The liquid environment is represented by an infinite polarizable continuum of the dielectric constant  $\epsilon(\omega)$ . Inside this continuum, there is an ellipsoidal cavity of dielectric constant  $\epsilon_c(\omega) = 1$ , into which the solute is placed. The charge distribution of the solute polarizes the continuum, which then creates an electric field that reacts back on the solute, that is the reaction field. For a given charge distribution, the interaction energy between the solute and the continuum can be written as

$$\langle H_{\text{cav}} \rangle = \frac{1}{2} \sum_{l,m=0}^{\infty} \Gamma_{lm} \langle Q_{lm} \rangle^2. \quad (7.1)$$

This can be derived from the equations governing the classical electrostatics of the model. The coefficients  $\Gamma_{lm}$  are the reaction field factors which depend entirely on the size and shape of the cavity and the dielectric constant of the continuum. The  $Q_{lm}$  are then related to the multipole moments of the charge distribution within the cavity. The angular brackets, in this case, denote quantum averages. This energy term can then be added to the Kohn–Sham energy functional and then, in the subsequent minimization, an additional term arises in the Fock matrix  $F_{\mu\nu} = F_{\mu\nu}^{\text{KS}} + F_{\mu\nu}^{\text{cav}}$ , which arises entirely from the cavity term above. The Fock equations are then solved, self-consistently, in the presence of the solvent, thus allowing for the electronic polarization of the solute by the solvent. This is the self-consistent reaction field method. The inclusion of analytical derivatives of the above term then allows geometry optimization, thus also allowing for the nuclear polarization effects of the solvent.

In our implementation of this model, we use an ellipsoidal cavity [119]. The dimensions of the cavity (i.e. its three semi-axes) are well defined within the model. They are related to the van der Waals radii of each of the atoms in the solute and an empirical relation between the total volume enclosed in the van der Waals surface of the molecule and the actual experimental molecular volume. Full details have been given in [119]. Since this defines the geometry of the cavity, this also, together with the dielectric constant, completely defines the reaction field factors in the above equation. We then include terms in the expansion up to and including the quadrupole, that is  $l = 2$ . These two factors, namely the shape of the cavity and the truncation of the multipole expansion, may seem to be a little careless since well developed models for a molecularly shaped cavity and inclusion of terms in the expansion of up to order  $l = 7$  already exist in the literature (see for example [118, 120]). Our reasoning for choosing the model that we have is as follows. As stated previously, the purpose of designing the MAGIC program is to enable the user to perform calculations reliably on large heavy-atom systems. These will involve large complexes, typically complexes that will have a very low symmetry. Thus, such systems will not have dominant high-order multipoles and the terms in the above expansion will monotonically decrease as one goes to higher and higher orders. Given this fact, a truncation at the quadrupole

term seems appropriate. Similar reasoning can also be applied to the use of the ellipsoid-shaped cavity since large complexes will typically have such a shape.

It is worth clarifying the physical content of the model since elaborations to the basic model do exist. Firstly, we have written the dielectric constant as having a frequency dependence. In this model we use the static permittivity or the zero-frequency dielectric constant as, for the moment, we are interested in the static properties of large heavy-atom systems, that is properties in which the dynamical response of the liquid to changes in the charge distribution of the solute are not particularly important. Two of the physical effects that have not been included are the free energy of cavity formation (cavitation energy) and the dispersion contribution to the interaction free energy. Both terms have been shown to be roughly constant with respect to changes in the geometry of the solute [120] and, therefore, as we shall be typically interested in geometries and energy differences, we expect that these terms will have a smaller contribution to such quantities than the more dominant electrostatic energy. Finally, the model that we have implemented, or any cavity model for that matter, will be most effective in situations where the interactions between the solute and the solvent are relatively weak, and, in particular, in cases where there is no chemical activity between the solute and solvent. In such cases, the solvent acts purely as an environment and it will more than likely induce *quantitative* changes in the potential energy surface of the solute, for example inducing a change in the barrier height to some sort of isomerization. Such a solvent can be said to be passive. The approximations made in such models will break down in the cases where the solute interacts strongly with the solvent, that is the solute interacts *chemically* with the solvent molecules in its immediate neighbourhood and chemical bonds between solute and solvent are formed. In these situations, the discrete nature of the liquid is of vital importance and, thus, the continuum approximation to the solvent breaks down. Here the solvent is active rather than passive. The potential energy surface of the solute now has *qualitative* changes. One can consider that the binding solvent molecules then become part of the solute and the whole complex forms a large supermolecule. If one wishes to continue to use continuum models in these situations, supermolecule calculations must be performed, with a large cavity containing the solute molecule and several solvent molecules. This sort of calculation has recently been performed in a study of the uranyl and plutonyl cations [121].

## 8. The code

Considering the complexity of the applications that are envisaged by the project, we have structured the MAGIC program in as transparent and easily extended way as possible. Further, the program needs to be as robust as we can make it while still allowing execution in a reasonable time. This latter requirement also includes minimizing the use of computer resources and, in particular, the efficient use of memory.

The starting point is the choice of computer language, although writing the code simply should make it possible to change this fairly easily. However, an initial choice of FORTRAN was made for the scientific programming. It is the relatively inflexible nature of this language leading to greater consistency, compared with C, as well as its general use throughout scientific programming, which prompted its choice. Some Cray extensions were used, in particular POINTER and MALLOC, where they offered advantages. Otherwise only standard features of the languages were used. For

those routines with a greater computer science connection, for example the input and output of the program, we chose to use C.

The main structure of the program is modular. Each module corresponds to a specific part of the model, for example building the DFT grid or adding the two-electron contribution to the Fock matrix, and is entirely self-contained. This allows these features of the model to be changed quickly by the amendment of the appropriate module. Although these modules may be executed individually, a single-point energy calculation is typically performed by a script which combines modules in a definite way. It is, of course, possible for users to construct their own individual scripts where required. Similarly, in collaborating with others to develop the program, they write their own module to perform the science and this is incorporated into a given procedure.

An important consideration of such a scheme is how the modules communicate, that is both receive data and output results. We would also like such results to be easily transferred among different users. To do this we use an archive facility within the MAGIC. This consists of a number of binary files which are written to the hard disk during execution of the program. These include both intermediate and final results. Simple instructions within the routines, namely put and get, write and retrieve named archive files. For example, the instruction 'call put ("molecule.centres", centres)' would write the contents of the array 'centres' to an archive file called 'molecule.centres'. This archive file may then be subsequently retrieved by another module. It is also convenient that the final results can be viewed from the archive making an output file redundant. One advantage of this approach is that the accuracy of display of the results may be easily adjusted by the access facility. It is then only necessary for different users to have the same archiving module in order to pass archive files between them.

Looking at the robust aspects of the code, we programmed each module as simply and consistently as we could. This should make it simpler for each programmer, either the original programmer looking back over a routine or a new programmer, to understand its computer science. This should also avoid undue repetition of existing code within the program. Emphasis is then placed on the science, where we want it. Each module is short (less than 1000 lines of code) and performs a clear task.

Although we initially made no approximations within our chosen model, we found this to be too slow for practical use. Therefore we introduced the following approximations. In the calculation of two-electron integrals we do not calculate integrals smaller than an input threshold. In the DFT module we do not calculate the values of basis functions less than a fixed threshold for batches of grid points. Again in the DFT we do not add contributions to the Fock matrix less than a fixed threshold. These approximations save considerable time in execution of the program, particularly for larger systems. It is clear that the threshold may be set to remove completely the approximation if required.

Mathematical library routines are widely used where possible in MAGIC. This removes the need for writing specific mathematical procedures, often much less efficiently or robustly than in existing libraries. It also helps to improve the portability of the program between machines.

One way to improve the efficiency of a program is to run it in parallel. We have developed a parallel version of the MAGIC program on a Cray T3E at the CINECA supercomputer centre in Italy. The message-passing interface has been used as it is the most portable of the existing parallelization methods. No Cray-specific instructions

have been used, making it equally applicable on a Silicon Graphics machine, for example. Work has been mainly concentrated in the two-electron and DFT routines, which are usually the most expensive in any calculation. Mathematical procedures, such as diagonalization, have been parallelized through the use of Scalapack through an easy-to-use interface. Other modules, such as the grid build, have been parallelized in a simple manner.

The development of the MAGIC code has been predominantly on Silicon Graphics computers, with the parallel version being developed on the Cray. The Casevision Visual Debug environment has been used, allowing the developer to check many aspects of the basic source code as work is in progress. Such tools make the development of a robust code more straightforward. When completed, a module is checked by running a collection of roughly 200 test decks. Thus we are able to verify that it is performing correctly and that it is not adversely affecting another part of the program.

### 9. Graphical user interface

The MAGIC program includes an interface to the molecular modelling package Cerius<sup>2</sup> [122]. After the initial selection of a study area (which is the directory in which all subsequent files will be kept), the user is then presented with a number of modules to run. Each module has its own panel from which appropriate options may be selected. When ready, the user simply clicks on the go button to run the module.

Within each panel there are a number of other features. On the right-hand side of each there are a number of help buttons. The first displays a general description of the module. Next there is a button to show the archive files read by the module. Further buttons show the archive files added, those required by a module for successful execution and the resources used.

It is also possible to use the MAGIC tools from the graphical user interface. These are similar to modules except that they do not write to the archive. Typically they read some archive information, use it as necessary and output the results directly to the user. Examples of such tools include 'Access', which displays the contents of an archive file.

Job control is handled from a panel. It allows calculations to be run in the foreground or background. They may be killed while running and results may be checked at intermediate points of the calculation.

Access to the other modules of Cerius<sup>2</sup> is very useful. These include the geometry sketcher, which is used to provide a rough starting geometry. An optimization with an empirical potential is usually run before beginning the MAGIC calculation.

### 10. Applications

The applications of the MAGIC project have been carefully chosen to give us information about both the model that we are using and the types of property that we may reasonably calculate to compare with experiment. The purpose of this section is to demonstrate our approach to calculating these properties of actinide complexes. We shall also discuss some example systems and the situations in which these occur. Where specific details have been published elsewhere a reference is given.

Our starting point is the uranium hexafluoride (UF<sub>6</sub>) molecule in the gas phase. There is a large amount of experimental information [123–127] about this molecule, providing us with comparative data. There have also been a number of other

theoretical studies [38, 39, 128–134]. This allows us to examine the relative accuracy of our methods.  $\text{UF}_6$  is important for the enrichment process of uranium and as such plays a key role in the nuclear industry [135, 136]. It is the feedstock for the production of  $\text{UO}_2$  ceramic nuclear fuel, made by the reaction  $\text{UF}_6 + 2\text{H}_2\text{O} + \text{H}_2 \rightleftharpoons \text{UO}_2 + 6\text{HF}$  via some intermediates that are not well understood. In order to compare and contrast the properties of similar complexes of different actinides, we next consider plutonium hexafluoride ( $\text{PuF}_6$ ). Although  $\text{PuF}_6$  is not currently used in any reprocessing process, it has historically been suggested that the separation of uranium, plutonium and fission products could be achieved by the same method as uranium-235 and uranium-238 separation. It is this separation process which involves the hexafluoride.

The calculations were then extended to include the dimers of both  $\text{UF}_6$  and  $\text{PuF}_6$ . The  $\text{UF}_6$  dimer has been suggested as one of the intermediates that occur in the production of  $\text{UO}_2$  ceramic nuclear fuel from  $\text{UF}_6$ . Our aim was to verify whether such an intermediate might possibly exist under the typical conditions of the fuel manufacture.

It is important that our applications should move towards the real-world systems that we ultimately wish to study. Therefore the next step was to move to small uranium and plutonium complexes. Our primary interest is in the relative stability of these complexes. In particular, we are interested in how the structure of the ligand affects the complex stability. The ligand chosen was thenoyltrifluoroacetone (TTA), which is based on the familiar acetylacetone (acac) ligand. We shall use it as a representative of the 1,3-diketone class of ligands. Experimental data are now restricted to some stability constants, with no previous theoretical work available. From the experimental data it is possible to derive a trend for the ease of extractions of different valence states of plutonium. It is this which will be compared with our theoretical results. At this point the detailed results become predictions.

Finally we present a discussion of some considerably more complicated uranium and plutonium complexes and the circumstances in which they are used. These systems tend to become more and more specific. For meaningful comparison with experiment and for reasonable prediction, it becomes increasingly necessary that the true system is modelled. For example, it may be necessary to include the fact that the complex is in solution.

### 10.1. Uranium and plutonium hexafluoride monomer and dimer

We performed a comprehensive study on the  $\text{UF}_6$  monomer which has been described in detail in [137]. The minimum energy as a function of the U–F distance, assuming octahedral symmetry, and the atomic energies, were determined at the following levels of theory:

- (1) in an all-electron non-relativistic calculation ALL (UF)-nr, by using an all-electron relativistic basis set on uranium and a non-relativistic basis set on fluorine;
- (2) by using a relativistic effective core potential (RECP) on uranium and a non-relativistic ECP on fluorine (RECP(U)-ECP(F));
- (3) by using a RECP on uranium and an all-electron non-relativistic basis set on fluorine (RECP(U)–ALL(F)).

Both the LDA and the BLYP functionals were used.

Turning to the dimer, we assumed that each monomer maintains  $O_h$  symmetry and that the dimer has  $D_{2h}$  symmetry. We are aware of the fact that in the real system the

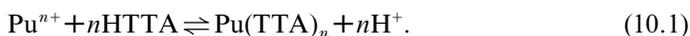
monomers might have a distorted geometry, but for this first investigation we considered the octahedral symmetry of each monomer and the  $D_{2h}$  symmetry of the dimer a reasonable approximation.

A more detailed discussion has been reported in [137]. The key conclusions of these investigations were as follows:

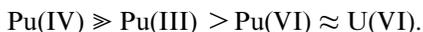
- (1) Atomization energies of both  $UF_6$  and  $PuF_6$  were predicted close to experiment when using ECPs on both the actinide and halogen. The experimental energies are 32.55 eV [123] and 28.86 eV [124] respectively. These compare with the calculated results of 33.92 eV and 29.58 eV using the LDA exchange functional.
- (2) Relativistic effects must be included (e.g. they lead to a 50% change in the calculated atomization energy of  $UF_6$ ). The calculated atomization energy of  $UF_6$  without relativistic effects was 23.11 eV.

### 10.2. Complexes of uranium and plutonium with thenoyltrifluoroacetone

The use of 1,3-diketones for the extraction and purification of actinides is a well established fact [135, 138, 139]. In the case of plutonium, a possible chelating species is 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione or TTA. Some ions in aqueous solutions are not extracted by organic solvents and may be converted into chelate compounds, which in turn are soluble in non-polar solvents, such as benzene, benzene derivatives or chloroform. Numerous compounds are also known that form chelate complex compounds which are extractable into organic solvents. 1,3-Diketones have been tested for possible application in an isolation process, in which a non-ionized chelate species is formed, which is then extracted into an organic solvent. The chelation reaction involved is given by the following equation



In the case of plutonium, the chelation of Pu(III), Pu(IV) and Pu(VI) involves three, four and two molecules respectively of TTA. From a study on the equilibrium constants [139], it turns out that the extractability of these species is determined by the series



In another paper [140] we present an extensive study on complexes of plutonium and TTA. In the following we describe in general terms the methods that we used to study these compounds and the typical properties that we are interested in. We performed energy calculations on the complexes and in some cases we estimated the solvent effect. We also optimized bond distances, with particular attention to the plutonium–ligand bonds. Although our models are a simplification of the real chemical processes, we think that an investigation of the electronic structure and properties of a number of molecules can provide useful information for a better understanding of the real chemistry of these compounds.

In most of the calculations the LDA exchange functional [112, 113] was used. Some comparative calculations were done including the correlation functional  $VWN$  and also the exchange–correlation BLYP [9, 10] functional. The relativistic effects are considered by the use of RECPs.

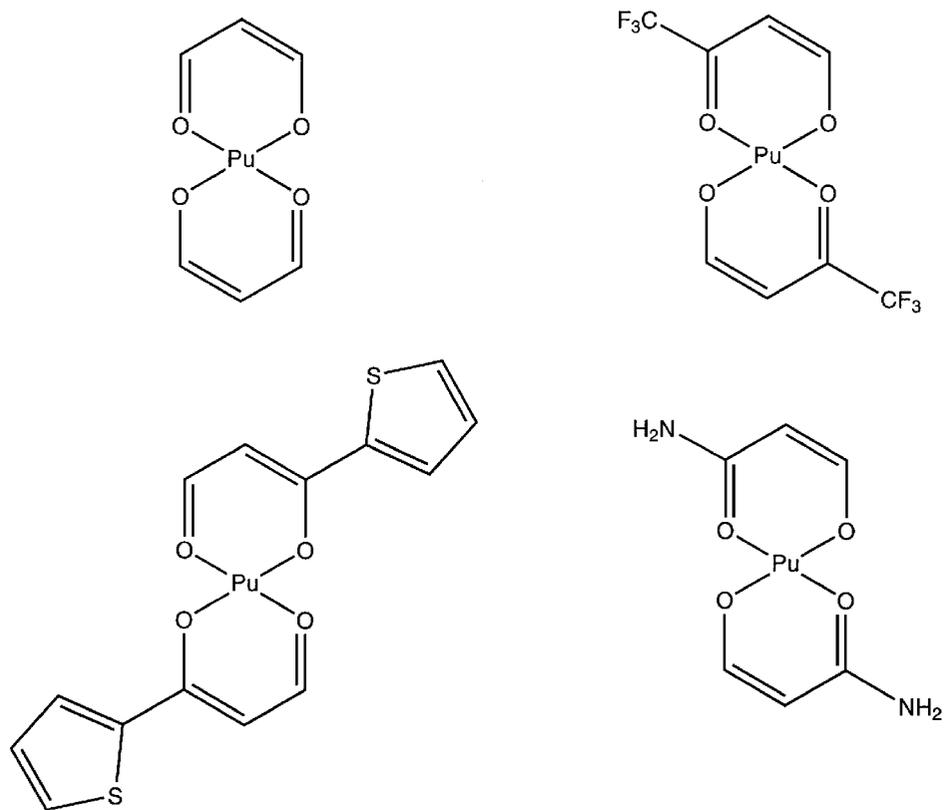


Figure 1.  $\text{Pu}(\text{L}1)_2$ ,  $\text{Pu}(\text{L}2)_2$ ,  $\text{Pu}(\text{L}3)_2$  and  $\text{Pu}(\text{L}4)_2$ .

The RECP employed on the uranium and plutonium atoms and the ECP on the fluorine atom are those reported by Hay [128, 141]. The valence basis set used to represent the 6s, 7s, 6p, 7p, 6d and 5f orbitals of uranium was the (10s8p2d4f) primitive contracted to [3s3p2d2f] and that of plutonium was the (12s10p2d4f) contracted to [3s3p2d2f], while on fluorine a (4s5p) primitive basis contracted to [2s2p] was employed, as reported in Hay's [128] paper. The all-electron basis used for the light atoms was the Dunning DZ [142], and for plutonium the uncontracted (24s19p16d11f) reported in [143]. The auxiliary basis sets for the light atoms were those optimized by Eichkorn *et al.* [144] for a split valence plus polarization [145] basis. For plutonium, since a specific auxiliary basis set does not exist, we used the rubidium auxiliary basis, reported in [144].

The initial geometry of the complexes was optimized by using the force field obtained by Rappe *et al.* [146] within the Cerius<sup>2</sup> package. We later optimized only the Pu–O (ligand) distances *ab initio*, but this made little difference to our results.

The properties that we looked at were both energetics and geometries, which were used to give an estimation of the relative stability of the different complexes. We analysed a number of different types of complex, as summarized by the following.

- (1) *Different actinide elements (uranium and plutonium).* The preliminary study involved plutonium. This was extended to include uranium so that a comparison could be made of the influence of the actinide on the stability of the complex.

Table 1. Examples of Pu(II) and Pu(VI) complexes:  $D_e$  is the difference between the energy of the complex minus the energy of plutonium (or  $\text{PuO}_2^{2+}$ ) and twice the energy of the ligand. The values are computed with the LDA exchange functional.

| System                              | $D_e$  |
|-------------------------------------|--------|
| $\text{PuO}_2^{2+} (\text{L2}^-)_2$ | 414.82 |
| $\text{Pu}^{2+} (\text{TTA}^-)_2$   | 287.58 |

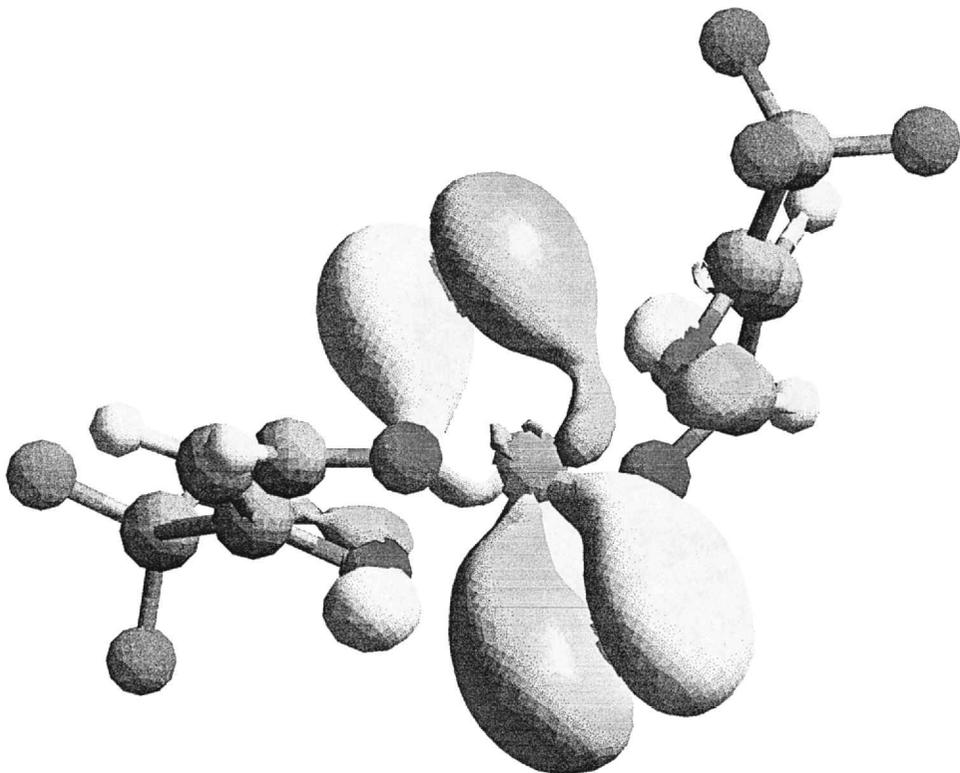


Figure 2. The HOMO of the  $\text{PuO}_2(\text{L2})_2$  complex.

- (2) *Different valence states of the actinides.* The order of extractability of the different valence states of plutonium is known from experiment. This is one of the few comparisons that we are able to make with experiment. We considered plutonium in its (II), (IV) and (VI) valence states. These contain two, four and two TTA ligands respectively.
- (3) *Different ligand structures.* We decided to examine the effect of the ligand structure on the stability of the complex. In particular we removed the side groups from the ligand in a systematic way. These are labelled L1, L2, L3 and L4 (figure 1). The ligand L1 does not contain a side group, L2 contains the electron-withdrawing  $\text{CF}_3$  group, L3 the electron-donating sulphur ring and L4 a different electron-donating group,  $\text{NH}_2$ . With these four ligands we formed the complexes of Pu(II). In table 1, some examples of results on these compounds are reported.

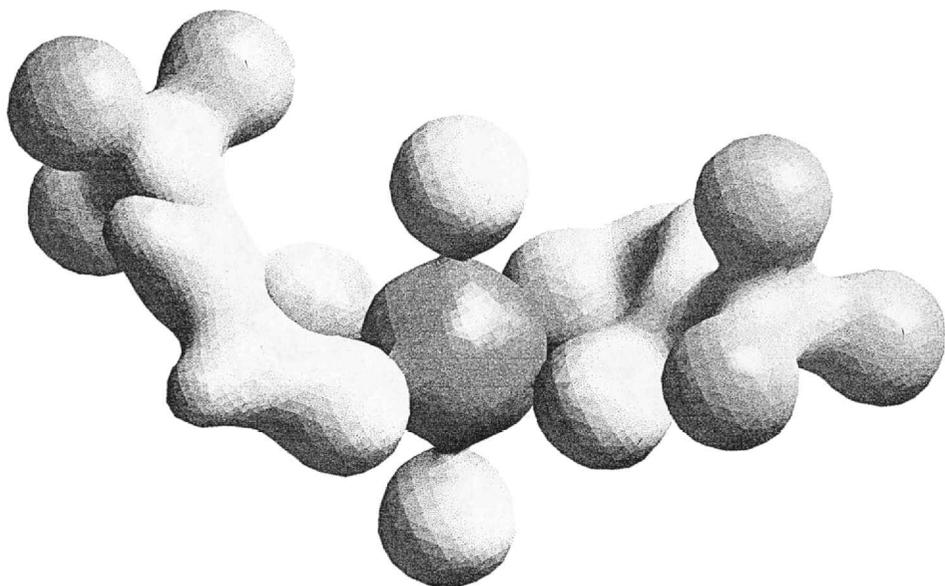


Figure 3. The electrostatic potential of the  $\text{PuO}_2(\text{L}2)_2$  complex drawn on a density isosurface.

- (4) *Different multiplicities of the actinides.* The similar energies of the HOMO and LUMO of the actinide elements lead to very small differences between the energies of different electronic configurations. We therefore decided to investigate the effect of this difference on our calculated complex stabilities.

The visualization of the results of an *ab initio* calculation becomes increasingly important as the complexity of the system increases. It helps considerably in the identification and subsequent discussion of the qualitative results of the calculation. Clearly a large number of different pictures may be produced and it is important that an appropriate choice of property is made. Three such pictures (figures 2–4) have been included for the  $\text{PuO}_2(\text{L}2)_2$  complex. The first shows a representation of the HOMO. We see that the atomic orbitals involved are those on the plutonium atom and the surrounding oxygen atoms. This may be used, for example, in explaining the nature of the bonding. The second picture shows the electrostatic potential on a density isosurface. We have included only the nuclear contribution. The areas of more negative potential are in the vicinity of the plutonium atom, moving towards smaller negative potential around the fluorine atoms. The third picture shows a slice through the electronic density. It should be remembered that, as the plutonium is represented by an ECP, only the valence density is shown. As expected, the areas of greatest density are in the vicinity of the atoms. Even given the use of an ECP, there is still considerable density about the plutonium atom. As we move further out, so the density decreases.

Our results all indicate that the complexes of uranium and plutonium with ligands based on a 1,3-diketone structure are very stable. The trend in stability of the complex when the ligand structure is changed parallels that of the known volatility of these compounds. The Pu(VI) and U(VI) valence states form considerably more stable complexes than the corresponding (II) valence states. The spin multiplicity of the actinide fragments was carefully considered and a number of calculations led to the use of the following: Pu(IV) and U(II) quintets; Pu(II) septet;  $\text{UO}_2^{2+}$  singlet;  $\text{PuO}_2^{2+}$  triplet.

Table 2. Examples of U(II) and U(VI) complexes:  $D_e$  is the difference between the energy of the complex minus the energy of uranium (or  $\text{UO}_2^{2+}$ ) and twice the energy of the ligand. The values are computed with the LDA exchange functional.

| System                             | $D_e$  |
|------------------------------------|--------|
| $\text{UO}_2^{2+} (\text{L}2^-)_2$ | 590.78 |
| $\text{U}^{2+} (\text{TTA}^-)_2$   | 423.54 |

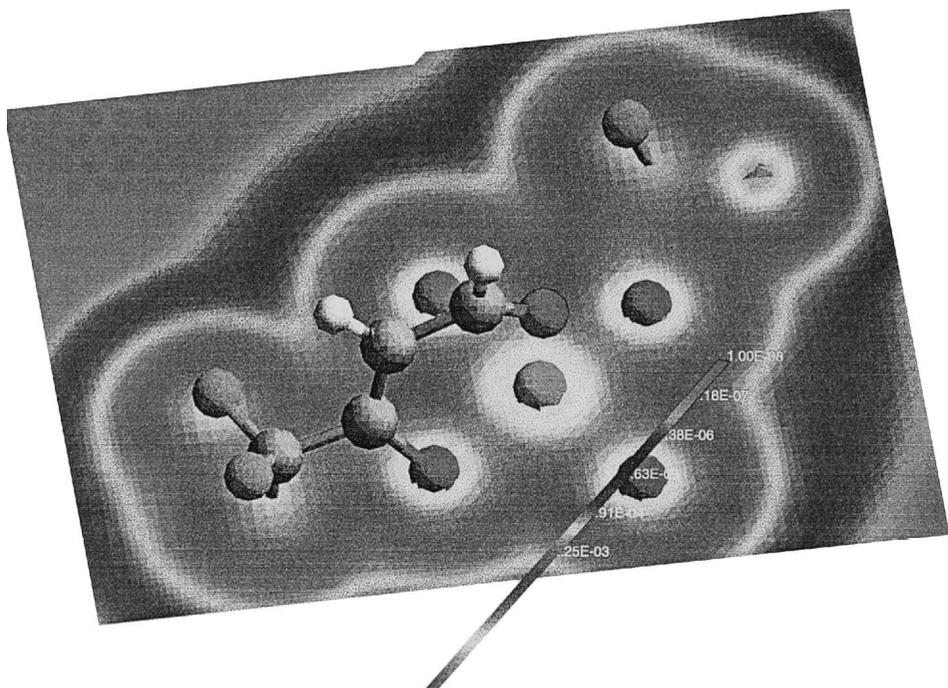


Figure 4. A slice through the electronic density of the  $\text{PuO}_2(\text{L}2)_2$  complex.

Some comparative calculations have been carried out on the analogous uranium complexes (table 2). The dissociation energies of  $\text{U}^{2+}(\text{TTA}^-)_2$  and  $\text{UO}_2^{2+}(\text{L}2^-)_2$  are shown at the LDA exchange functional level. We expect the LDA to overestimate the binding energy of these compounds. In general we notice that the Pu–U(VI) compounds are more stable than the Pu–U(II) compounds are. Among the Pu(II) compounds, those with the electron-donating groups ( $\text{Pu}^{2+}(\text{L}3^-)_2$  and  $\text{Pu}^{2+}(\text{L}4^-)_2$ ) were found to be more stable than that with the electron-accepting group  $\text{Pu}^{2+}(\text{L}2^-)_2$ . Further, comparing the plutonium and uranium results, the uranium compounds seem to be more stable than the plutonium compounds. These are only preliminary results and a complete investigation which includes a basis set superposition error estimation and a proper geometry optimization of the complexes has been given [140].

We are currently investigating also Pu(IV) which seems to form stable complexes [147]. The coordination number is generally eight in Pu(IV) complexes. A qualitative assessment of the idealized geometry of an eight-coordinated plutonium complex is often described in terms of cubic distortion, forming polyhedra of lower energy, which closely resemble a dodecahedron, square antiprism or bicapped trigonal prism [147].

### 10.3. *Towards real chemistry: some plutonium complexes of biochemical interest*

Initially, one of the primary aims of MAGIC is to assess the suitability of complexants for the solvent extraction process. To this end, MAGIC is able to calculate energies of complexes formed between organic ligands and the various cations, such as the uranyl or plutonyl ions. The need to extract actinide elements occurs not only in fuel reprocessing technology but also in areas such as medicine. Our examples of still larger and more complex ligands include some plutonium complexes of biochemical interest. These were chosen partly because they represent an interesting area of actinide extraction and partly because the ligands need to be highly specific.

Although the actinide elements have no essential role in the normal biochemical reactions which occur in plants, animals or man, a knowledge of their interactions with the various constituents of cells and tissues is important for the understanding of the mechanisms which control their specific tissue deposition pattern, for the initiation of toxic effects and for the development of methods for treating people who may become contaminated with actinides. The reactions of the actinides with various components of mammalian blood, cells and tissues have been the subject of a number of publications [135, 136, 147].

Because it is the most abundant actinide produced in the fission nuclear fuel cycle, and because it is now present in minute quantities in our normal environment, the biochemistry of plutonium has been more widely studied than that of any other actinide. Chelation therapy for the removal of plutonium following contamination has been the subject of a number of reviews [136, 147, 148, 149]. Several compounds have been proposed as chelating agents. Ethylenediaminetetraacetate (EDTA) is certainly one of the most common for all metals in general. As regards its use with the actinides, the  $[\text{Th}(\text{H}_2\text{O})_2(\text{EDTA})]$  and  $[\text{U}(\text{H}_2\text{O})_2(\text{EDTA})]$  complexes have been isolated. Potentiometric pH titrations and ion-exchange and spectrophotometric studies show that stable 1 : 1 metal chelates are formed with Pu(III), Pu(IV), Pu(VI) and  $\text{Pu}(\text{VI})\text{O}_2^{2+}$ .

The chelating agent diethylenetriaminepentaacetate (DTPA) is the therapeutic of choice for actinide decorporation therapy. DTPA is an extremely hydrophilic molecule and its effectiveness will depend upon its ability to chelate the actinide from transferrin. Formation constants for the interaction of DTPA with some actinides elements are available [136] and it turns out that DTPA is expected to be effective in chelating plasma protein bound actinide. In fact, DTPA is able to reduce the body burden of most of the actinides. From this discussion it seems obvious that DTPA is most effective against actinides present in plasma.

At the present stage we are running calculations on complexes of plutonium with both EDTA and DTPA. These examine both the nature of the bonding and its strength. This is the first step in our goal of engineering new ligands for the specific extraction of particular actinide elements.

## 11. The future

The MAGIC project is about the use of computational methods to predict the properties of actinide systems in the real world. Assuming this, the future of the project may involve the following areas of research.

- (1) Applications must be made on systems with a greater resemblance to those in current use at British Nuclear Fuels plc. The systems that we have presented in this paper have proved useful in defining where in a complicated mathematical

model problems may arise. These may be inadequacies in the model or simply to do with the way that the model has been implemented. It is mainly through the study of more and more complicated systems that we shall move the project forwards. We have tried to choose systems where comparison with experiment or other theoretical calculations is possible. Otherwise, any predictions that we have made have been cautiously stated. The true usefulness of such an approach, however, will be when the results are accurate enough to be used for prediction. In this way, much experimental effort may be saved.

- (2) Improvement in the existing theoretical models is required to give better results for a wider range of systems. For example, we may well imagine the use of a relativistic functional. This also carries on directly from comment (1), in that it is only through inclusion of accurate solvent and radiation effects, for example, that we may hope to make good predictions.
- (3) Predictions of the properties of these systems beyond those currently calculated are needed. Examples of such properties include those involving reaction kinetics.
- (4) When developing a computer program for such a project it is important that the main focus, that is the applications, is kept a priority. However, it is inevitable that we have also carefully considered the structure of the program. From the viewpoint of the code developer, we have made the program as transparent as we could. There is, however, always further work to do in this area, as new ideas come to mind. This is also true of the end user, where it is through the use of the program by a number of people that its interface will develop.

In summary, the MAGIC project attempts to use existing quantum chemistry methods to look at very complicated systems. Careful consideration of the computer program allows the user and developer to concentrate on the science, and not necessarily the computer science.

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