

# Relativistic quantum mechanical methods in molecular calculations<sup>☆</sup>

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## Abstract

In the present paper the theory for different relativistic methods is presented. Despite a lot of progress has been made for the inclusion of relativistic effects in electronic structure calculations, good methods are still resource-demanding. A rapid development of the four-component method is, however, taking place. Also, “pseudo-relativistic” approaches are becoming more popular in the treatment of large systems. The importance of the interplay between the relativistic core and valence effects is also revisited.

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## 1. Introduction

Over the last decade, a lot of progress has been made in the development of efficient and accurate algorithms for the inclusion of relativistic effects in electronic structure calculations [1]. In essence, the approaches can be divided into those that are ‘truly’ relativistic, in the sense that they operate with quantities which are or almost are invariant to a Lorentz transformation, and those that attempt to incorporate the main effects of relativity on physical observables into a more or less non-relativistic formalism. While the former approach is clearly the more accurate one it is also more computationally demanding. Lately, methods based on the four-component Dirac equation have enabled the study of heavy systems with impressive accuracy for even medium size molecules [2,3]. This method is still relatively resource-demanding and for larger systems more effective approximate methods have been developed. A rapid development of the four-component method is, however, taking place and

a competition with more simplified methods may be seen in a not too remote future [4].

There is, however, still a demand for methods that lend themselves to large systems, an increasing amount of evidence shows encouraging numerical results from these ‘pseudo-relativistic’ approaches and they are increasingly popular and can be incorporated into non-relativistic schemes, drawing on the vast realm of computational experience and development of codes and algorithms.

Since relativistic behaviour is associated with fast-moving, i.e. core electrons, it is natural to look for effective core potentials which incorporate those effects. Such RECP methods have been available for quite a long time [5,6] and have been applied with success to a spectrum of problems.

Quite often, however, the chemistry of interest is associated with phenomena in the valence region, and the interplay between the relativistic core and valence effects is not always well accounted for with a core potential. All-electron models therefore are a high priority, perhaps even more so than in non-relativistic work, especially when spin–orbit are taken into account.

For cases where the total relativistic effects are small, they can be treated as a perturbation on a non-relativistic system, and in an essentially non-relativistic formalistic framework. These pseudo-relativistic methods have been applied with some success. However, they fail miserably (as expected) for a number of cases where relativity brings about major changes in the wave function, which need to be accounted for

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<sup>\*</sup> Professor Odd Gropen passed away in February 2005. He wrote this paper in honor of Professor Ramon Carbó-Dorca and his outstanding contribution to Theoretical Chemistry and Molecular Simulation.

at the zeroth order level. In the present paper, the theory for different relativistic methods will be presented.

## 2. The four-component theory

All theories are based on the Dirac equation or the Dirac–Coulomb equation. We will therefore start by presenting the basic theory. The Dirac equation for the free electron has the following expression

$$i \frac{\partial \Psi}{\partial t} = H_D \Psi \quad (1)$$

where

$$H_D = (c\boldsymbol{\alpha}p + \beta mc^2) \quad (2)$$

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{bmatrix} \beta = \begin{bmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{bmatrix} \beta \quad (3)$$

where  $\boldsymbol{\sigma}$  are the (2·2) Pauli matrices

$$\boldsymbol{\sigma} = \left( \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) \quad (4)$$

As the Dirac operator thus contains 4×4 matrices it is only meaningful to assume that the wave function is a four-vector, or a four-component *spinor*:

$$\Psi = \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{bmatrix} \quad (5)$$

The Dirac equation for the hydrogen atom takes the following form including the external potential

$$H_{\text{ext}}^D \Psi = E \Psi \quad (6)$$

$$H_{\text{ext}}^D = \boldsymbol{\alpha}p c + \beta mc^2 - \frac{Z}{r} \quad (7)$$

In matrix form

$$\begin{bmatrix} (mc^2 - Z/r)\mathbf{I} & \boldsymbol{\sigma}p c \\ \boldsymbol{\sigma}p c & (-mc^2 - Z/r)\mathbf{I} \end{bmatrix} \begin{bmatrix} \Psi^{(+)} \\ \Psi^{(-)} \end{bmatrix} = E \begin{bmatrix} \Psi^{(+)} \\ \Psi^{(-)} \end{bmatrix} \quad (8)$$

where

$$\Psi^{(+)} = \begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix}, \quad \Psi^{(-)} = \begin{bmatrix} \Psi_3 \\ \Psi_4 \end{bmatrix} \quad (9)$$

The equation for the many-electron system takes the following form

$$H\Psi = E\Psi \quad (10)$$

where

$$H = \sum_{i=1}^n H_{\text{ext}}^D(i) + \sum_{i<j} V_{ij} \quad (11)$$

$$H_{\text{ext}}^D(i) = \boldsymbol{\alpha}p_i c + \beta mc^2 - \sum_{\mu} \frac{Z_{\mu}}{|\mathbf{r}_i - \mathbf{R}_{\mu}|} \quad (12)$$

$$V_{ij} = \frac{1}{r_{ij}} - \frac{1}{2r_{ij}} \left\{ \alpha_i \alpha_j + \frac{(\alpha_i r_{ij})(\alpha_j r_{ij})}{r_{ij}^2} \right\} \quad (13)$$

It should be noted that the two-electron term in this ‘Dirac–Coulomb’ equation is based on a classical (i.e. non-relativistic) picture of the interaction; and it is therefore *not* Lorentz invariant.

Solving the four component equations always give two sets of solutions. One set, the so called large component solutions, corresponding to electronic states has energies near  $E \approx mc^2$  and the following relations  $\Psi^{(-)} \approx c^{-1} \Psi^{(+)}$  between  $\Psi^{(-)}$  and  $\Psi^{(+)}$ . The other solutions are called the small component solutions and correspond to the positron solutions. They have energies near  $E \sim -mc^2$  and the following relations  $\Psi^{(+)} \approx c^{-1} \Psi^{(-)}$  between  $\Psi^{(-)}$  and  $\Psi^{(+)}$ .

In computational chemistry, we are interested in the electronic states, which unfortunately exist as excited states in the continuum for the positron states and have to be projected out from the total space. The minimax theorem for excited states requires, however, that the lower lying states have to be well described to avoid a collapse of the excited states. That means among other things that with a complete basis set of the positron states the electronic states will converge as usual from above with increasing basis for these states, whereas with a complete set for the electronic states they will converge from below to the correct values with increasing basis set for the positron states. This has been discussed by many authors [7–9]. Complete basis sets are, however, an unrealistic requirement, and it was early recognized that a balance between the small and the large component would give reasonably good results [10].

The requirement on the small component basis given a large component basis may be deduced from the Dirac equation to the following relations:

$$\Psi_i^{(3)} = \frac{-1}{2c[1 - (E - V)/2c^2]} \left\{ \frac{\partial}{\partial z} \Psi_i^{(1)} + \left( \frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) \Psi_i^{(2)} \right\} \quad (14)$$

$$\Psi_i^{(4)} = \frac{-1}{2c[1 - (E - V)/2c^2]} \left\{ \frac{\partial}{\partial z} \Psi_i^{(2)} + \left( \frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) \Psi_i^{(1)} \right\} \quad (15)$$

In a usual way we may apply the LCAO approach, expanding the molecular spinor in a set of atomic spinors

$$\Psi_i = \sum_{\mu} k_{\mu}^i \phi_{\mu} \quad (16)$$

$$\phi_{\mu}^{L\alpha} = \begin{pmatrix} \chi_{\mu}^{L\alpha} \\ 0 \\ 0 \\ 0 \end{pmatrix}, \phi_{\mu}^{L\beta} = \begin{pmatrix} 0 \\ \chi_{\mu}^{L\beta} \\ 0 \\ 0 \end{pmatrix}, \phi_{\mu}^{S\alpha} = \begin{pmatrix} 0 \\ 0 \\ \chi_{\mu}^{S\alpha} \\ 0 \end{pmatrix}, \phi_{\mu}^{S\beta} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \chi_{\mu}^{S\beta} \end{pmatrix} \quad (17)$$

At this point it is clear that one may proceed as in the non-relativistic approach. Choosing an independent particle model with an antisymmetric wave function represented by a Slater determinant one obtain the Dirac Fock equations. Based on this one-electron basis CI, CCSD(T) and DFT procedure may be developed. The logistics and the fact that complex algebra is applied make in addition to a larger basis this method more demanding than the non-relativistic procedure. There exist, however, efficient programs that carry out such calculations, and they may be obtained for free [4].

### 3. Decoupling of the electronic and positron solutions

The first major steps towards a computationally useful pseudo-relativistic variational approach were taken by Sucher [11], who developed the approach usually known as the ‘no-pair’ (NP) method. The method attempts to eliminate positronic states through a unitary transformation, the form of which is derived from the Dirac equation for an electron without external field. The name is related to the quantum electrodynamic approach used in the original derivation and justification of the approach. (It is a bit surprising that this works at all, since the effects of interest here are precise those caused by the presence of a very strong external field!)

As the coupling between electronic and positronic states is eliminated the latter can be removed from further consideration. The equations involved are thus reduced in complexity, from the original four-component problem to one including only two components. (In the non-relativistic limit these two components correspond to the  $\alpha$ - and  $\beta$ -spin of a single, free electron—in relativistic theory these states are no longer pure and well separated.)

The Hamiltonian for the free electron is the only Hamiltonian that may be decoupled exactly. However, using the free electron transformation, the so called NP transformation, for molecular systems we obtain a substantial reduction of the off diagonal matrix elements in the operator, and by neglecting these small contribution we obtain electronic states decoupled from the positron states

obtaining the following operator:

$$H_+ = \sum_{i=1}^n (E_i + V_{\text{eff}}(i)) + \sum_{i<j} V_{\text{eff}}(i,j) \quad (18)$$

$$E_i = (m^2 c^4 + p^2 c^2)^{1/2} \quad (19)$$

$$A_i = \left( \frac{E_i + mc^2}{2E_i} \right)^{1/2} \quad (20)$$

$$Q_i = \frac{c\sigma_i p_i}{(E_i + mc^2)^{1/2}} \quad (21)$$

$$U_{ij} = \left\{ \alpha_i \alpha_j + \frac{(\alpha_i r_{ij})(\alpha_j r_{ij})}{r_{ij}^2} \right\} \quad (22)$$

$$V_{\text{eff}}(i) = A_i [V_{\text{ext}}(i) + Q_i V_{\text{ext}}(i) Q_i] A_i \quad (23)$$

$$V_{\text{eff}}(i,j) = A_i A_j \left[ \frac{1}{r_{ij}} + Q_i \frac{1}{r_{ij}} Q_i + Q_j \frac{1}{r_{ij}} Q_j + Q_i Q_j \frac{1}{r_{ij}} Q_i Q_j \right] A_i A_j \\ + A_i A_j [U_{ij} Q_i Q_j + Q_i U_{ij} Q_j + Q_j U_{ij} Q_i + Q_i Q_j U_{ij}] A_j A_i \quad (24)$$

where  $V_{\text{ext}}(i)$  is the usual, non-relativistic one-electron potential,

$$V_{\text{ext}}(i) = \sum_{\mu} \frac{Z_{\mu}}{|\mathbf{r}_i - \mathbf{r}_{\mu}|} \quad (25)$$

The original four-component Dirac–Coulomb Hamiltonian has thus been reduced to the two-component Hamiltonian  $H_+$ . One of the virtues of this method is that  $H_+$  can be further divided into a spin-free and a spin-dependent part. Using the Dirac relation

$$(\boldsymbol{\sigma}u)(\boldsymbol{\sigma}v) = uv + i\boldsymbol{\sigma}(u \cdot v) \quad (26)$$

to separate spin and space coordinates, the complete operator is finally obtained ignoring the spin–spin part:

$$H = \sum_{i=1}^n (E_i + V_{\text{eff}}^{\text{sf}}(i) + H^{\text{SO}}(i)) + \sum_{i<j} (V_{\text{eff}}^{\text{sf}}(i,j) + H^{\text{SO}}(i,j)) \quad (27)$$

$$V_{\text{eff}}^{\text{sf}}(i) = A_i [V_{\text{ext}}(i) + \mathbf{R}_i V_{\text{ext}}(i) \mathbf{R}_i] A_i \quad (28)$$

$$H^{\text{SO}}(i) = B_i \sum_{\mu} \frac{Z_{\mu}}{|\mathbf{r}_i - \mathbf{r}_{\mu}|^3} \boldsymbol{\sigma}_i(\mathbf{r}_i \cdot \mathbf{p}_i) B_i \quad (29)$$

$$V_{\text{eff}}^{\text{sf}}(i,j) = A_i A_j \left[ \frac{1}{r_{ij}} + \mathbf{R}_i \frac{1}{r_{ij}} \mathbf{R}_i + \mathbf{R}_j \frac{1}{r_{ij}} \mathbf{R}_j + \mathbf{R}_i \left( \mathbf{R}_j \frac{1}{r_{ij}} \mathbf{R}_j \right) \mathbf{R}_i \right] A_i A_j \quad (30)$$

$$H^{\text{SO}}(i,j) = - \left( B_i A_j \frac{1}{r_{ij}^3} (\mathbf{r}_{ij} \cdot \mathbf{p}_i) \boldsymbol{\sigma}_i B_i A_j + 2 B_j A_i \frac{1}{r_{ij}^3} (\mathbf{r}_{ij} \cdot \mathbf{p}_i) \boldsymbol{\sigma}_j B_i A_j \right) \quad (31)$$

$$\mathbf{R}_i = \frac{\mathbf{p}_i c}{mc^2 + E_i}, B_i = \frac{c A_i}{E_i + mc^2} \quad (32)$$

The necessity of the spin-free complicated two-electron term has been a discussion in the literature [12,13]. No clear conclusion has been drawn, but this operator is usually reduced to the well known and simple two-electron contribution

$$V_{\text{eff}}^{\text{sf}}(i,j) = \frac{1}{r_{ij}}$$

While the resulting calculations are relatively straightforward, the results are unfortunately poor. In a refinement of the approach, Douglas and Kroll [14] suggested additional transformations. Normally, the DK refinement is carried only through second order, and only for the one-electron part of the Hamiltonian (for details see for example Ref. [1]). The resulting, extra term becomes:

$$H_{\text{eff}}^{\text{DK}}(i) = -\frac{1}{2} \{ \{ E_i, W_1^{\text{sf}}(i) \}, W_1^{\text{sf}}(i) \} \quad (33)$$

where  $W_1$  is an integral operator with the kernel

$$W_1(\mathbf{p}_i, \mathbf{p}'_i) = A_i [Q_i - Q'_i] A'_i \frac{V_{\text{ext}}(\mathbf{p}_i, \mathbf{p}'_i)}{E_i - E'_i} \quad (34)$$

and  $V_{\text{ext}}(\mathbf{p}_i, \mathbf{p}'_i)$  is the Fourier transform of the external potential.

Some literature distinguishes between the no-pair approach and the Douglas–Kroll method (DK), here, we will consider NP as a ‘first-order DK’ treatment and these methods will all be referred to as the DK approach.

The computational implementation of the DK methods by Hess et al. [15–18] has gained a lot of attention and has been applied with success to a large number of chemical problems. In cases where spin is not a major issue (closed-shell systems, not extremely heavy elements), one can often neglect the latter and work in a spin-free formalism.

The structure of this spin-free, one-component Hamiltonian is thus the same as in non-relativistic theory, and this structural ‘isomorphism’ can be used to take advantage of the vast experience and code development for non-relativistic calculations. One-component, ‘pseudo-relativistic’ calculations may be done on an almost a routine basis. The inclusion of spin–orbit interaction is far more complicated [19]. We will return to these complications below. The DK methods should be contrasted to e.g. the Breit–Pauli approach, which is essentially a perturbation expansion where the zeroth order Hamiltonian is furnished by non-relativistic case and the effect of relativity is treated as a perturbation. This operator is obtained with among other methods by the Foldy–Wouthuysen transformation [20]. For a one-electron system, the Breit–Pauli Hamiltonian is given by

$$H^{\text{BP}} = mc^2 + H_{\text{nr}} + H_{\text{mv}} + H_{\text{Dar}} + H_{\text{SO}} + \dots \quad (35)$$

where the terms are the well known non-relativistic, the mass velocity, the Darwin and the one electron spin orbit term. The  $H_{\text{mv}} + H_{\text{Dar}}$  terms are often used as perturbation contribution for spin free calculations, whereas

the spin–orbit interaction term

$$H^{\text{SO}}(i,j) = -\left( \frac{1}{r_{ij}^3} (\mathbf{r}_{ij} \cdot \mathbf{p}_i) (\boldsymbol{\sigma}_i + 2\boldsymbol{\sigma}_j) \right) \quad (36)$$

may be used as a perturbation for spin–orbit if this contribution is small.

BP has many similarities with DK theory, and the BP Hamiltonian can indeed be obtained from DK through series expansion and truncation. However, in actual applications they behave quite differently. The DK method has been found to provide a variationally stable effective Hamiltonian, and can thus be used in variational calculations. This is an important advantage over BP Hamiltonians, which can only be used in perturbation calculations. The basic reason for this is the expansion of the kinetic energy in the BP operator. This gives a non converging series with alternating terms.

#### 4. Integrals in Douglas–Kroll theory

While the kinematic factors have a stabilizing effect on the behaviour of the various operators in DK theory, they at the same time make the numerical procedure more complicated. Using the LCAO approximation in ab initio electronic structure theory, one must evaluate large numbers of one- and two-electron integrals of the basis functions over various operators, but they can all be obtained analytically. This is not the case in the DK formalism. The kinematic factors make the operators complicated numerically.

The only known way to calculate integrals over the DK spin–orbit operator is to use the method of resolution of identity. This method is only correct if the expansion is taken in an infinite basis. It is, however, shown that using a relatively large primitive basis to expand the identity operator works well for all systems studied so far. With standard integral programs one should then calculate all the necessary integrals in a large primitive basis and then carry out a four-index transformation into the correct integrals and then a contraction to a usable basis. This method is easily handled for the one-electron part, but for the two-electron part this is a prohibitive approach for all but relatively small systems.

In addition to this complications, the spin-same orbit contribution and the spin other contribution have a different form

$$H^{\text{SO}}(i,j) = (B_i A_j \mathbf{L}_{ij} s_i B_i A_j + 2B_j A_i \mathbf{L}_{ij} s_j B_i A_j) \quad (37)$$

In order to simplify the two-electron DK spin–orbit term we may now define a new operator as the mean of the two terms above

$$H^{\text{SO}}(i,j) = (G_i G_j (\mathbf{L}_{ij} (s_i + 2s_j))) G_i G_j \quad (38)$$

Expanding the resolution of identity operator in the primitive basis a matrix element over this two-electron DK

spin-orbit operator in the contracted basis will take the following form

$$\begin{aligned}
 & (\phi_i(1)\phi_j(1)|\phi_k(2)\phi_l(2)) \\
 &= \sum_p \sum_q \sum_r \sum_s \sum_\mu \sum_\nu \sum_\sigma \sum_\lambda C_p^i C_q^j C_r^k C_s^l G_p^\mu G_q^\nu G_r^\sigma G_s^\lambda \\
 & \times (\phi_\mu(1)\phi_\nu(1)|\phi_\sigma(2)\phi_\lambda(2))
 \end{aligned} \quad (39)$$

It is reasonable to assume that the important part of the two-electron spin-orbit operator is a one centre term. The necessary expansion of the resolution of the identity should then also come from one centre. Taking this assumptions into consideration the  $G$ -matrix will be block diagonalized over basis functions with same  $l$ -quantum numbers on the same centre. We may then do the four inner summations resulting in a new set of contraction coefficients,

$$\begin{aligned}
 D_q^i &= \sum_p C_p^i G_p^q \\
 &= \sum_\mu \sum_\nu \sum_\sigma \sum_\lambda D_\mu^i D_\nu^j D_\sigma^k D_\lambda^l (\phi_\mu(1)\phi_\nu(1)|\phi_\sigma(2)\phi_\lambda(2))
 \end{aligned} \quad (40)$$

These new contraction coefficients may easily be constructed before the calculation of the two-electron spin-orbit matrix and a ordinary integral program may be used without any further restriction. An other simplification is the introduction of the mean-field operator [21].

$$\begin{aligned}
 H_{ij}^{\text{so}} &= \langle i|H^{\text{so}}(1)|j\rangle + \frac{1}{2} \sum_K n_k \{ \langle ik|H^{\text{SO}}(1,2)|jk\rangle \\
 & - \langle ik|H^{\text{SO}}(1,2)|kj\rangle - \langle ki|H^{\text{SO}}(1,2)|jk\rangle \}
 \end{aligned}$$

This has been done, and was implemented in the AMFI [22] code known as RASSI in the MOLCAS program system [23].

The spin-orbit contribution is usually included through perturbation or configuration interaction. A direct CI-procedure using a one-electron basis from a non-relativistic calculation was developed in our group and is briefly discussed here. The reference calculation producing the one-electron basis is always important for the quality of the CI-calculation. In non-relativistic calculations, the one-electron basis may be optimized for the state that is to be investigated, whereas that is usually not the case in spin-orbit calculations as a  $j$ -state is generally a mixture of two different L-S states. This weakness in the method may be remedied on the CI level including excitations that allow a rotation of the one-electron orbitals. This problem has not been given sufficient attention.

When CI calculations are carried out including the spin-orbit term we try to describe both the correlation energy and the spin-orbit energy. This may be done in two ways. Correlated calculations may be done on the separated L-S states followed by a short CI-expansion including

the spin-orbit operator and using the CI L-S states as expansion functions. This approach assumes a negligible coupling between correlation energy and the spin-orbit energy. The other possibility is a full CI including the spin-orbit term of the operator. The full CI treatment is a very resource demanding approach and may only be applied to relatively small systems. For most problems the non coupling approach is sufficient and the matrix to be diagonalized will have the following form with the size depending on the problem at hand:

$$\begin{aligned}
 & (H_{\text{el}} + H_{\text{so}})\Psi \\
 &= E\Psi \begin{bmatrix} E_{\text{el}}(\Psi_1) & \langle\Psi_1|H_{\text{so}}|\Psi_2\rangle & \langle\Psi_1|H_{\text{so}}|\Psi_3\rangle \\ \langle\Psi_2|H_{\text{so}}|\Psi_1\rangle & E_{\text{el}}(\Psi_2) & \langle\Psi_2|H_{\text{so}}|\Psi_3\rangle \\ \langle\Psi_3|H_{\text{so}}|\Psi_1\rangle & \langle\Psi_3|H_{\text{so}}|\Psi_2\rangle & E_{\text{el}}(\Psi_3) \end{bmatrix} \xrightarrow{\text{diagonalize}}
 \end{aligned} \quad (41)$$

But even with this limited approach the calculation of the spin orbit matrix elements may be substantial if large CI expansions are used. We have therefore suggested that the spin-orbit calculations may be carried out with a rather limited correlation, viz. small CAS calculations and the correlation effect may then be included through the inclusion of a so called effective Hamiltonian [24] which will only effect the diagonal elements

$$\begin{aligned}
 H_{\text{SO}}^{\text{eff}} &= H_{\text{SO}} + \sum_i \Delta E_i |\Psi_i\rangle\langle\Psi_i| \\
 \Delta E_i &= (E_i^{\text{corr}} - E_{\text{GS}}^{\text{corr}}) - (E_i^{\text{ini}} - E_{\text{GS}}^{\text{ini}})
 \end{aligned} \quad (42)$$

This is for most systems a satisfactory way of treating spin-orbit and correlation. But some cases require a full treatment where spin-orbit and correlation are treated on an equal footing. In those cases, it may be better to apply the full four-component method.

There are rapidly accumulating results from relativistic calculations, both four-component and the more approximate two component and the scalar methods. There is no results included here, only references to the literature [25–29]. Relatively large systems of chemical interest may be treated with one or all of these methods and the methodological development have made the lower part of the periodic Table accessible to theoretical studies. Especially the lanthanides and the actinides may now be studied theoretically [30–33]. These elements are of great interest both for catalyses and for the nuclear waste problems.

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