Numerical investigations of different orders of relativistic effects in atomic shells

K. Molzberger, W.H. Eugen Schwarz

Theoretische Chemie, Universität Siegen, D-57068 Siegen, Germany;
Fax: (+ 49)271-740-2330

Summary. Different orders in α^2 of the hydrogenic energy levels are discussed. The spurious contribution of $-0.2Z^5\alpha^3$ of the first order Douglas–Kroll–Hess (DKH) Hamiltonian is cancelled at the second order DKH level, which recovers the energy up to the order of $Z^6\alpha^4$ at least to a large extent and includes also a significant part of the higher order terms. Concerning the valence shell energies of many electron atoms, their behavior is more similar to the one of the hydrogen-like $1s$ than of the respective nlj levels. The convergence of the α^2 expansion becomes unsatisfactory for the very heavy elements.

Key words: Relativistic effects – Douglas–Kroll–Hess approach – Heavy elements

1 Introduction

Instead of solving the relativistic wave equation directly, one may choose a perturbation approach, which may computationally be more efficient [1]. Besides the Pauli–Foldy–Wouthuysen expansion (PFW) [2] several other perturbation methods have been developed in recent years such as the Direct Relativistic Perturbation Theory (DPT) [3, 4], the Regular Approximation (RA) [5], the Douglas–Kroll–Hess transformation (DKH) [6], etc. While the different orders of the PFW and DPT approaches correspond to different powers of α^2 in the energy expression (α: Sommerfeld's fine structure constant), the other approaches are equivalent to partial summations of the α^2-expansion.

For hydrogen-like *one-electron systems* with point nucleus of charge Z, the energy expression is known explicitly [7]. It is then possible to derive explicit expressions for the different orders in α^2 of the energy in the PFW or DPT approach, as well as in the RA approaches (zeroth order ZORA, first order FORA, etc.) [5, 8]. Concerning the DKH approach, it is probably impossible to derive *explicit* α-expansions (except for the zeroth order DKH energy). Therefore, the first aim of this note is to *numerically* investigate the α^n-expansion of the lower order DKH approximations for the energy of hydrogen-like ions.

As is well known, the relativistic corrections of the orbital energies of neutral, *many-electron atoms* differ drastically from those of the hydrogen-like ones [9]. Many-electron systems can only be treated by numerical methods. The magnitudes

of different orders of the relativistic contribution to valence shell energies must therefore be estimated on the basis of numerical power expansions. This is the second aim of this note.

2 Hydrogen-like systems

2.1 Dirac energies

The standard energy expression of hydrogen-like ions reads [7]

$$E_{nk} = [\{1 + \gamma^2/(n + \sqrt{k^2 - \gamma^2} - k)^2\}^{-1/2} - 1]/\alpha^2, \tag{1}$$

where n is the principal quantum number, $k = j + 1/2$, $j = l \pm 1/2$, and $\gamma = Z\alpha$. Expanding Eq. (1) in a power series of γ yields for the fractional relativistic energy correction

$$\varepsilon_{nk} = (E_{nk} - E_{nk}^{nonrel})/E_{nk}^{nonrel} = a(\gamma) \cdot \gamma^2 = a_2 \cdot \gamma^2 (1 + a_4 \cdot \gamma^2 (1 + a_6 \cdot \gamma^2 (1 + \cdots))) \tag{2}$$

with

$$a_2 = (n - 0.75\,k)/kn^2,$$

$$a_4 = (n^3 + 3kn^2 - 6k^2n + 2.5k^3)/(4n - 3k)\,k^2n^2,$$

$$a_6 = [8n^4(n + 3k) + 8k^2n^2(n - 15k) + 5k^4(24n - 7k)]/8$$
$$\times [2n^2(n + 3k) + k^2(5k - 12n)]\,k^2n^2,$$

$$a_8 = 5[n^6(n + 3k) + k^2n^4(2.4n - 8k) + 2k^4n^2(21k - 9n)$$
$$+ 7k^6(0.9n - 4k)]/[8n^4(n + 3k) + 8k^2n^2(n - 15k)$$
$$+ 5k^4(24n - 7k)]\,k^2n^2, \tag{3}$$

etc. which converge for $n \to \infty$ to $a_2 = 0$, $a_4 = 0.25/k^2$, $a_6 = 0.5/k^2$, $a_8 = 0.625/k^2$. (Of course, the first relations of Eq. (3) can be found at many places in the literature, e.g. [10]). $a_2\gamma^2$ is the percentage contribution of the first order correction to the nonrelativistic energy, $a_4\gamma^2$ is the percentage contribution of the second order correction to the first order relativistic energy term, and so on.

Typical values of γ^2 are 0.03 for Cr, 0.09 for Mo, 0.17–0.27 for the lanthanides and 0.42–0.56 for the actinides. For the $1s$ level, $n = k = 1$, of hydrogen-like systems one obtains $a_2 = 0.25$, $a_4 = 0.5$, $a_6 = 0.625$, $\cdots$. We note that the order of magnitude of the fractional relativistic effects in the valence shells of many-electron atoms and molecules is comparable to the one in the K shell of one-electron atoms. Therefore, as a rough rule of thumb, to obtain the energy with an accuracy of about 1%, the first order (i.e. a_2) is needed from the transition metals onwards; the second order (a_4) is needed from the lanthanides onwards; and the third order (a_6) should be included for the actinides (compare a similar discussion in [10]).

Numerical values for the a_i-coefficients are presented in Table 1. For given angular momentum (k, j or l) the a_i grow at first for increasing n, but then converge towards *smaller* values. a_2 even converges to zero, i.e. the relativistic correction vanishes for high quantum numbers. For increasing order i, the a_i increase. The second and third order energies, i.e. up to α^4 and α^6, respectively (DPT2 and DPT3), are compared with the Dirac energies in Fig. 1. It shows that, if higher order terms are needed, then one must cope with slow convergence, and methods

Table 1. Coefficients a_i (up to 4 digits) of the fractional relativistic energy corrections [see Eq. (2)] for hydrogen-like systems

$k(\ell j)$	n	a_2	a_4	a_6	a_8
$1(s\frac{1}{2})$	1	0.25	0.5	0.625	0.7
$1(sp\frac{1}{2})$	2	0.3125	0.525	0.6384	0.7083
	3	0.25	0.4753	0.6041	0.6840
	4	0.2031	0.4351	0.5772	0.6659
	5	0.17	0.4059	0.5589	0.6543
	6	0.1458	0.3843	0.5463	0.6468
	∞	0.0	0.25	0.5	0.625
$2(p\frac{3}{2})$	2	0.0625	0.125	0.1562	0.175
$2(pd\frac{3}{2})$	3	0.0833	0.1343	0.1614	0.1783
	4	0.0781	0.1312	0.1596	0.1771
	5	0.07	0.125	0.1553	0.1740
	6	0.0625	0.1188	0.1510	0.1710
	∞	0.0	0.0625	0.125	0.1562
$3(d\frac{5}{2})$	3	0.0278	0.0556	0.0694	0.0778
$3(df\frac{5}{2})$	4	0.0365	0.0590	0.0712	0.0789
	5	0.0367	0.0596	0.0717	0.0793
	6	0.0347	0.0583	0.0709	0.0787
	∞	0.0	0.0278	0.0556	0.0694
$4(f\frac{7}{2})$	4	0.0156	0.0312	0.0391	0.0438
$4(fg\frac{7}{2})$	5	0.02	0.0328	0.0398	0.0442
	∞	0.0	0.0156	0.0312	0.0391
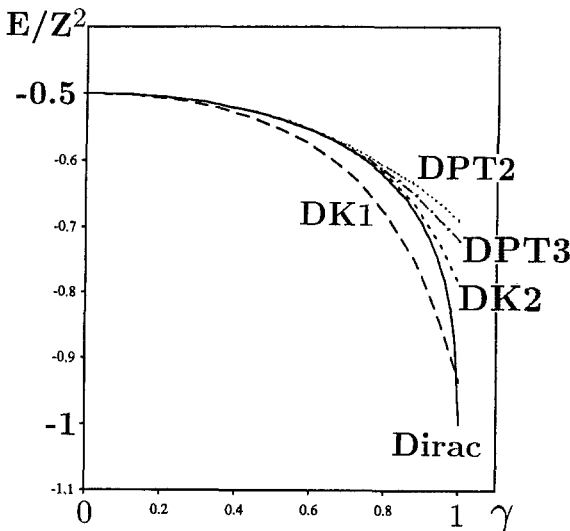
Fig. 1. E/Z^2 versus $\gamma = Z\alpha$ for hydrogen-like ions. —— Dirac, – – – first order DKH, - - - - - second order DKH, ··· ··· ··· second order DPT, ·—·—·— third order DPT (note that the latter orders here refer to γ^2, while some authors count orders of γ, i.e. what is denoted here by DPT3 is sometimes called DPT6)

which partially sum up the γ^n-series of the DPT approach may be preferable, such as the regular approximation or the Douglas-Kroll-Hess approach.

Concerning the regular approximation, we note that the zeroth order (called ZORA or CPD0) [5, 8] yields the following γ-expansion coefficients for hydrogen-like systems:

$$a_2^{\text{ZORA}} = a_2 + 1/4n^2,$$

$$(a_2 a_4)^{\text{ZORA}} = a_2(a_4 + 1/2n^2) + 1/16n^4,$$

etc. which differ appreciably from the exact Dirac values a_i of Eq. (3), especially for small quantum numbers. In the case of the "scaled ZORA" [8b, 24], however, which corresponds to the exact summation of all higher order terms in a purely Coulombic field, the exact Dirac expansion coefficients are of course recovered, $a_i^{\text{scaled ZORA}} = a_i$.

2.2 DKH energies

The idea of the DKH (and the RA) approach [6, 8] is to take special care of the strongly relativistic behavior of the electrons near the Coulomb singularity of the nucleus. The one-electron Hamiltonian may be written in the form

$$H^{\text{DKH}} = (\sqrt{m^2 c^4 + p^2 c^2} - mc^2 + V) + \Delta^{(1)} V + \Delta^{(2)} V + \cdots. \tag{4}$$

The zeroth order term H^{DK0} (the terms in parentheses) consists of the classical relativistic kinetic energy expression and the unmodified nuclear potential. The lowest order correction term is obtained by applying the iterative Douglas-Kroll transformation once [11]:

$$\Delta^{(1)} V = (AVA - V) + B\pi V\pi B$$

with

$$A = \{[1 + (1 + \wp^2)^{-1/2}]/2\}^{1/2} \approx 1 - \wp^2/8 + 11\wp^4/128 - \cdots,$$

$$B = \{[1 + (1 + \wp^2)^{1/2} + \wp^2]2\}^{-1/2} \approx 1/2 - 3\wp^2/16 - \cdots,$$

and

$$\wp = p/mc, \qquad \pi = \vec{\wp}\,\vec{\sigma}.$$

$\Delta V^{(1)}$ represents the Darwin correction to the electron-nuclear attraction and the spin-orbital coupling, though not in the non-variational, singular Pauli-Foldy-Wouthuysen form but in a screened form which is variationally stable. This approximation had been suggested by Hess and by Almlöf in 1985 [11, 12].

We have numerically diagonalized the zeroth, first and second order DKH Hamiltonians in extended Gaussian basis sets, for all Z-values from 1 to 130 (Fig. 1) thereby extending the numerical accuracy of Hess and Buenker [6, 11, 23]. The numerical $1s$ eigenvalues were then fitted to a polynomial in Z and α, using the technique described in Ref. [12]. For the zeroth order, i.e. the so-called square root equation, we obtain Sucher's result [22],

$$E_{1s}^{\text{DK0}} = -0.5Z^2 (1 + 1.250\gamma^2 (1 - 1.34\gamma^1 (1 \cdots))), \tag{5a}$$

for the first-order Douglas-Kroll-Hess equation

$$E_{1s}^{\text{DK1}} = -0.5Z^2 (1 + 0.250\gamma^2 (1 + 1.6\gamma^1 (1 \cdots))), \tag{5b}$$

for the second-order one

$$E_{1s}^{DK2} = -0.5Z^2 (1 + 0.250\gamma^2 (1 + 0.45\gamma^2 (1 \cdots))), \qquad (5c)$$

while the Dirac equation yields

$$E_{1s} = -0.5Z^2 (1 + 0.250\gamma^2 (1 + 0.50\gamma^2 (1 + 0.625\gamma^2 \cdots))), \qquad (5d)$$

and ZORA

$$E_{1s}^{ZORA} = -0.5Z^2 (1 + 0.500\gamma^2 (1 + 0.625\gamma^2 (1 \cdots))). \qquad (5e)$$

More expansion terms and more significant figures could not be obtained by the numerical fitting. The last digits in Eqs. (5a–c) are not exact. The problem is that at low values of γ, the higher order terms become negligibly small, while at high γ-values the convergence of the power expansions is too slow.

The singularity of the Coulomb potential introduces problems if combined with the classical relativistic kinetic energy expression, as at the DK0 level [14, 22]. The lowest order relativistic correction coefficient is $1.25\gamma^2$ [Eq. (5a)], as to be expected for a spinless particle [7b], instead of $0.25\gamma^2$ for the hydrogenic electron [Eq. (5d)]. The next term in Eq. (5a) is of odd order in γ, while the correct energy expression (5d) contains only even powers of γ. The numerical value of -1.34 agrees well with Sucher's analytical one, $-64/15\pi = -1.36$ ([22], compare the discussion in [14]).

The first order DKH Hamiltonian recovers the lowest order relativistic correction of $0.25\gamma^2$ exactly. Also the odd-order term is improved, though the first order DKH correction overshoots: the energy contribution of $+0.84Z^5\alpha^3 = 0.5Z^2 \cdot 1.25\gamma^2 \cdot 1.34\gamma$ according to Eq. (5a) is reduced to $-0.2Z^5\alpha^3$ according to Eq. (5b). The survival of a term of odd order is clearly demonstrated in Fig. 2a. There, $(E^{DK1} - E)/\gamma^3 E$ behaves approximately as $a - b \cdot \gamma$. Because of the γ^3 term, E^{DK1} is too low for medium Z-values (see Fig. 1).

The second order Douglas–Kroll–Hess operator cures the spurious γ^3-term and recovers the γ^4-term, viz. to about 90% within the numerical accuracy of the applied basis set expansion method. The stabilizing (i.e. negative) higher order energy contributions of the Dirac energy are not completely recovered by the DK2 approach (see Fig. 2b). Anyhow Fig. 1 shows that the DK2 approach is a significant improvement over the second and even third order DPT approach for high γ, i.e. high nuclear charges. Numerical calculations on the hydride of element 111 ($\gamma = 0.81$) by Hess et al. [15] indicate, indeed, that the DK2 approach is still sufficient.

3 The 6sp-valence shell of heavy many-electron atoms

While the fractional relativistic energy correction of an electron in a Coulomb field roughly behaves as $+n^{-1}k^{-1}$ [see Eqs. (2) and (3)], it is known from the classical work of Desclaux [9] that the behavior is quite different for electrons in a screened Coulomb field, such as in many-electron atoms. Within one column of the periodic table the fractional relativistic correction for ns orbital energies in *valence shells* does not at all decrease as n^{-1} (see Table 2), and for the average $np_{1/2,3/2}$ orbital energies it has even a negative sign (relativistic destabilization) except for the elements in the lower right corner of the periodic table (I and Bi to Rn). The d- and f-orbitals are relativistically destabilized, too, in many-electron atoms [9, 16, 17].
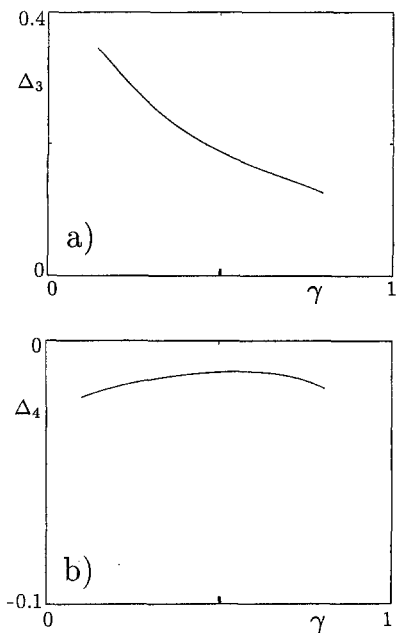
Fig. 2. Fractional relativistic energy corrections of first and second order DKH approaches. (a) Top: $\Delta_3 = (E_{1s}^{DK1} - E_{1s})/\gamma^3 E_{1s}$ versus $\gamma = Z\alpha$. E_{1s}^{DK1} is the hydrogenic $1s$-energy of the first order DKH Hamiltonian, E_{1s} is the Dirac energy. (b) Bottom: $\Delta_4 = (E_{1s}^{DK2} - E_{1s})/\gamma^4 E_{1s}$ versus $\gamma = Z\alpha$

Table 2. Coefficients a of the fractional relativistic energy corrections of valence shell orbital energies [see Eq. (3)] of the neutral atoms in the periodic table from Dirac–Fock calculations [8]

Group	1	2	11	12	13	14	15	16	17	18
$2s$	0.17	0.20			0.32	0.40	0.44	0.48	0.51	0.53
$3s$	0.20	0.20			0.29	0.34	0.37	0.39	0.40	0.42
$4s$	0.20	0.19	0.68	0.44	0.45	0.44	0.44	0.44	0.44	0.44
$5s$	0.22	0.20	0.66	0.51	0.50	0.48	0.47	0.46	0.45	0.45
$6s$	0.23	0.21	0.97	0.75	0.70	0.66	0.63	0.60	0.59	0.57
$2p^a$					− 0.26	− 0.21	− 0.18	− 0.16	− 0.15	− 0.14
$3p^a$					− 0.19	− 0.14	− 0.12	− 0.09	− 0.08	− 0.07
$4p^a$					− 0.13	− 0.08	− 0.06	− 0.04	− 0.03	− 0.02
$5p^a$					− 0.10	− 0.06	− 0.03	− 0.02	− 0.01	− 0.00
$6p^a$					− 0.06	− 0.02	0.01	0.02	0.04	0.05

[a] Weighted average of $p^{1/2}$ and $p^{3/2}$. These values were completely misprinted in [9]

It is sometimes stated that relativistic corrections in the valence shells are caused indirectly due to orthogonality of the "nonrelativistic" valence orbitals on the "relativistic" inner core orbitals. The above-mentioned behaviors are an indication against this opinion. Furthermore, Rose et al. [18] have demonstrated that valence orbitals are modified directly by relativistic kinematics of their inner tails, and by the relativistically enhanced nuclear shielding leading to non-hydrogen-like relativistic destabilization. In addition it has been shown that the orthogonality of the valence orbitals on the relativistically *contracted* inner core shells does not result in the naively anticipated valence orbital contraction, but in a (comparatively small) *expansion* [19].

In conclusion, it is a nontrivial question how the total valence shell energies of heavy atoms are relativistically modified, and how much the different orders of γ^n contribute. In order to answer these questions, numerical Dirac–Fock calculations were performed on neutral atoms and positive ions with a Pt core and $6s^0$, $6s^2$, $6s^2 6p_{1/2}^2$ or $6s^2 6p_{1/2}^2 6p_{3/2}^4$ valence shells. The nuclear charge (Z) was varied from 80 to 90, the velocity of light (c) from $\alpha^{-1} = 100$ to ∞. (The *total* energies of rare gas atoms were investigated in this manner by Davidson et al. [20].) Slater's approximation was used here for the exchange terms. Since relativity/exchange-correlation cross-terms are in general not dominant effects, we may expect the results still to be semiquantitatively correct.

The valence shell energies are defined as follows:

$$E_{val.}^c = E_{config.1}^c - E_{config.2}^c, \tag{6}$$

for instance, config.1 = $[Pt]s^2 p^2$, config.2 = $[Pt]s^2$, and val. = p^2. The fractional relativistic energy corrections are then defined as in Eq. (2):

$$\varepsilon_{val.} = (E_{val.}^c - E_{val.}^{c=\infty})/E_{val.}^{c=\infty} = a_2 \gamma^2 (1 + a_4 \gamma^2(1 + \cdots)). \tag{7}$$

Some numerical results are presented in Table 3. The order of magnitude of a_6, which could not be determined with any reasonable accuracy, ranges from 0.2 to 1. For two typical cases, the $6s^2$ and the $6p_{3/2}^4$ shells, $\varepsilon_{val.}/\gamma^2$ is plotted versus $\alpha^2 = 1/c^2$ in Fig. 3.

The fractional relativistic stabilization of the $6s^2$ two-electron shell is smaller than the one of the $6s$ one-electron orbital, while the opposite holds for the $6p_{1/2}^2$ and $6p_{3/2}^4$ shells in comparison to the $6p_{1/2}$ and $6p_{3/2}$ orbitals (note the difference

Table 3. Coefficients a (for $c = 137$), and expansion terms a_2 and a_4 (last digit is questionable) of the fractional relativistic energy corrections of valence shell energies [Eqs. (6), (7)] and of orbital energies (a^{orb}) from Dirac–Slater calculations

Shell	Atom	a	a_2	a_4	a^{orb}	
$6s^2$	Hg^0	0.613	0.451	0.7	$6s$:	0.917
	Pb^{2+}	0.380	0.291	0.65		0.405
	Rn^{6+}	0.279	0.217	0.5		0.280
	Th^{10+}	0.248	0.191	0.5		0.247
$6s^2 6p_{1/2}^2$	Pb^0	0.364	0.274	0.7		
	Rn^{4+}	0.264	0.205	0.6		
	Th^{8+}	0.236	0.182	0.5		
$6p_{1/2}^2$	Pb^0	0.310	0.223	0.7	$6p_{1/2}$:	0.296
	Rn^{4+}	0.241	0.186	0.6		0.239
	Th^{8+}	0.221	0.170	0.5		0.220
$6s^2 6p^6$	Rn^0	0.166	0.127	0.6		
	Th^{4+}	0.140	0.109	0.5		
$6p^6$	Rn^0	0.069	0.051	0.6		
	Th^{4+}	0.076	0.061	0.5		
$6p_{3/2}^4$	Rn^0	− 0.120	− 0.099	0.5	$6p_{3/2}$:	− 0.360
	Th^{4+}	− 0.032	− 0.020	1.0		−0.051
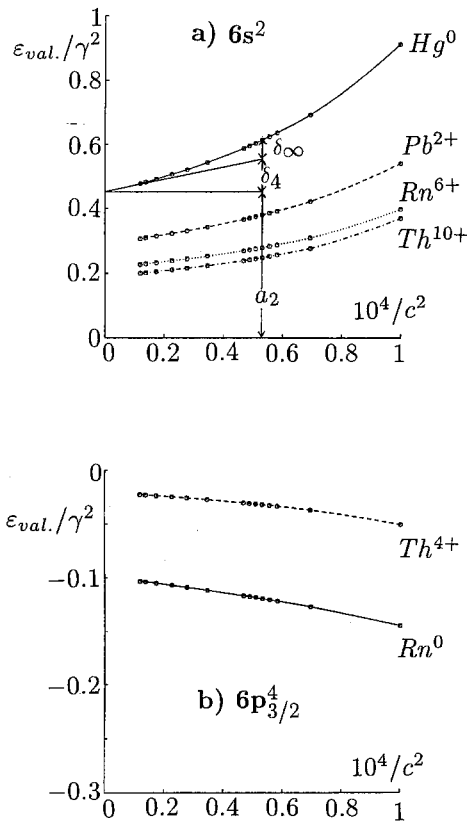
Fig. 3. $\varepsilon_{\text{val.}}/\gamma^2$ versus $10^4/c^2$, where $\varepsilon_{\text{val.}}$ is the fractional relativistic correction of the valence energy, see Eqs. (6), (7), at the Dirac–Fock–Slater level; $\gamma = Z\alpha = Z/c$. (a) Top: $6s^2$ shell of Hg^0, Pb^{2+}, Rn^{6+}, Th^{10+}. a_2 is the lowest order relativistic correction coefficient, δ_4 and δ_∞ indicate the second order relativistic term, and the higher orders, respectively (for Hg and $c = 137$). (b) Bottom: $6p^4_{3/2}$ shell of Rn^0 and Th^{4+}

between the Dirac–Fock orbital energies in Table 2, and the Dirac–Slater orbital energies in Table 3, which have different physical meanings).

The proportionality coefficients a of the fractional relativistic effects along an isoelectronic series decrease for increasing nuclear charge. This means, the fractional relativistic effects are especially large for "soft" valence shells.

Comparing a_2 with a we see that the lowest order contributes about 75% to the total relativistic energy of the valence shells for atoms with $Z = 80$–90. The second order a_4-term contributes about 15–20%, and the higher orders 5–10%. This is sketched in Fig. 3a.

4 Conclusions

The relativistic effects in the valence shells result from the interplay of two effects [17–19]. First there is the relativistic kinematics of the inner tails of the valence orbitals, the so-called direct relativistic effect. It is much larger in the screened Coulomb field of many-electron atoms than in the hydrogen-like pure Coulomb field. Second, there is the electron repulsion due to the relativistically modified charge distribution, which is called the indirect relativistic effect (having nothing to do with orthogonality constraints) or the relativistic shell effect or the relativistic

nuclear screening. Since the two effects are different for different orbitals, and since the one- and two-electron terms contribute differently to one-electron orbital energies and to total valence-shell energies, one must be very careful when drawing conclusions about the relativistic effects of a many-electron system on the basis of a one-electron (e.g. Hückel type) MO model.

The importance of the relativistic higher order contributions decreases with increasing principal and angular momentum quantum numbers in the hydrogenic case. This is not the case for the valence orbitals of real atoms. Their a_i coefficients are, roughly speaking, of a similar order of magnitude as the hydrogenic ones for the $1s$ state. For many chemical purposes, the nonrelativistic approximation works up to $Z \sim 25$ (first transition metals), and the first order relativistic correction $\sim \gamma^2$ up to $Z \sim 75$ (first post-lanthanides). For slightly larger Z-values, however, also the second order relativistic correction $\sim \gamma^4$ becomes insufficient because the higher order contributions become comparable. Accordingly, in order to achieve high accuracy, the second order relativistic terms must be included for medium heavy atoms, but to achieve medium accuracy for very heavy atoms, methods are needed which also cover orders in γ even higher than γ^6, at least partially.

The Douglas-Kroll-Hess approach partially sums up the different relativistic orders. Concerning the so-called first order DKH approach, it is still contaminated with spurious terms of order $\sim \gamma^3$. Indeed, the first-order DKH approach has been applied rather seldom, e.g. in [11, 12, 21]. The γ^3-error is cured at the second order DKH level. Numerical calculations for hydrogenlike $1s$-levels show that the error of the latter approach remains very small up to $Z \sim 120$.

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