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REGULAR ARTICLE

Relativistic effects in low-lying electronic states of iron

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Abstract Excited electronic states of Fe I have been calculated using the MRCI Douglas–Kroll–Hess method. Average spin-free excitation energies of the eight lowest even electronic terms ($a^5D, a^5F, a^3F, a^5P, a^3P2, a^3H, b^3F2$, and a^3G) are reported. The RASSI method was employed for calculation of individual *J* levels of the four lowest terms. All reported values are in good agreement with experiment. Our study pointed out significant relativistic effects even in relatively light element like iron.

Keywords Fe I · Excitation energies · Relativistic effects · Spin–orbit interactions · RASSI · MRCI

1 Introduction

The importance of relativistic effects in understanding general trends of molecular properties within the Periodic Table was generally recognized in the late seventies and early eighties. A milestone to this topic was brought by a pioneering work of Pyykkö and Desclaux [1] followed by other reviews on the development of the relativistic quantum theory of many-electron systems and its applications to atomic and molecular properties [2–8]. Clearly, relativity is present in all elements in the Periodic Table but its importance increases for systems in which participate elements with high enough atomic number. While writing a recent review on relativistic effects in atomic and molecular properties [8], we have returned to our earlier work [9] on the iron atom and its excitation energy from the ground ^5D state to the first excited state ^5F, using the coupled cluster CCSD(T) method for the treatment of the electron correlation. With the simplest relativistic mass-velocity-Darwin (MVD) approach, the relativistic contribution to the excitation energy (EE) was 0.282 eV representing 28% of the final CCSD(T) value, 1.025 eV. Upon extending and supplementing the basis set with spherical *g*-functions, the excitation energy was improved to 0.981 eV, still quite far from the experimental value 0.859 eV [9, 10]. Similar enhancement of EE due to relativistic effects, 0.26 eV, was observed before by numerical nonrelativistic and relativistic Hartree–Fock calculations of Martin and Hay [11]. Their final value, 2.06 eV, is too high due to the neglect of electron correlation effects. Similar effect of relativity at the level of the MVD approximation follows also from configuration interaction calculations with single and double excitations (CISD) [12], which leads to EE of 1.06 eV.

This paper is dedicated to Pekka Pyykkö, a pioneer of relativistic quantum chemistry, on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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Even though considering the electron correlation reduces the difference between the theoretical and experimental EE considerably, there seems to be much space for improving the agreement of theoretical EE with experiment. First, there are available advanced theoretical tools for simultaneous treatment of both relativistic and electron correlation effects [5–8]. Second, there are systematically optimized relativistic basis sets [13, 14] for calculations of electron affinities, ionization potentials, and excitation energies of the 3*d* transition metal atoms for highly correlated CC and multireference configuration interaction methods (MR CI). These basis sets, designed for extrapolations to the complete basis set (CBS) limit, were optimized having in mind the treatment of scalar relativistic effects using the Douglas–Kroll–Hess (DKH) method [15–17]. Particularly important are nonrelativistic and relativistic ANO basis sets [18, 19] optimized for MR CI, CASSCF (complete active space SCF), and second-order perturbative CASPT2 calculations. These basis sets are suitable for considering the spin–orbit energy levels by the restricted active space state interaction method (RASSI) proposed by Roos and Malmqvist [20, 21].

For accurate description of the ground and excited states of the iron, atom spin–orbit (SO) states and the multitude of states must be treated simultaneously at highly correlated level. In some states, the theoretical and experimental description is complicated by a strong mixing of states [10, 22]. To obtain a realistic description of the levels of Fe, both dynamic and nondynamic correlation effects must be included at the relativistic level [23, 24]. It is interesting to note that accurate calculations of the transition frequencies of Fe may contribute to the search for the space–time variation of the fine structure constant in quasar absorption spectra [22]. To achieve this goal, Dzuba and Flambaum have developed a special many-multiplet method [25] designed for systems with strong mixing of several distinct configurations.

The purpose of this paper is twofold. First, we wish to have a closer look at relativistic effects on several states of Fe at the spin-free relativistic DKH level. Usually, more attention is paid to the transition between the ground ^{5}D state having the electron configuration [Ar]$3d^64s^2$ to the first excited state ^{5}F and other states with the electron configuration [Ar]$3d^74s^1$. Along with such states, we will treat excited states that have the same electron configuration as the ground state. This will allow the understanding of trends in relativistic effects for a variety of states characterized by these two basic electronic configurations of Fe. Furthermore, we will also calculate LS states arising from a multitude of [Ar]$3d^64s^2$ and [Ar]$3d^74s^1$ electronic configurations, respectively, relying on CASSCF, MR CI, RASSI, and the averaged coupled-pair functional (ACPF) methods as implemented in the MOLCAS system [20, 21, 26].

2 Methodology

2.1 Spin-free calculations

The first and most demanding step in this project were spin-free (SF) calculations of accurate excitation energies of the three lowest quintet and five lowest triplets electronic states of the iron atom.

In order to avoid symmetry broken solutions, we had to decrease the computational symmetry to C_i, which enables orbitals with the particular angular momentum to occupy the only one particular representation. The CASSCF method with the (8/6) active space was used to describe the static electron correlation. The active space comprised 4*s* and 3*d* orbitals, and all possible roots within this space were evaluated, i.e., 15 roots for the quintet spin multiplicity and 105 roots with the triplet multiplicity. This rather unusual large number of roots was necessary particularly for triplet states where higher excited states lie close to each other [10], and the dynamic correlation could change their ordering.

The effect of the dynamic electron correlation was treated with the multireference configuration interaction (MRCI) method with single and double excitations. Here, the orbital space was divided as follows: 1*s*, 2*s*, 2*p*, and 3*s* orbitals were set as frozen, 3*p* orbitals were inactive, and the active space was the same as in the CASSCF part, 4*s* and 3*d* orbitals. For each root corresponding to the examined electronic state, the separate MRCI calculation was made. We used two different corrections that were added to the final MRCI energy to achieve its size extensivity. Namely, the Davidson correction labeled here as CI + Dav [26, 27] and the averaged coupled-pair functional (ACPF) correction [26, 28] labeled here as CI + ACPF.

The ANO–L basis set [18, 26] in the vQZP contraction has been used for nonrelativistic calculations. The ANO–RCC basis set [19, 26] in the vDZP, vTZP, vQZP, and so-called large contraction was used for scalar relativistic calculations within the Douglas–Kroll–Hess formalism [15–17]. Thus, the largest basis of this set consisted of (21*s*15*p*10*d*6*f*4*g*2*h*)/[10*s*9*p*8*d*6*f*4*g*2*h*] functions. Let us add that the software used in our calculations is the Molcas 7 package of electronic structure programs [26].

2.2 spin–orbit calculations

The spin–orbit energy levels were computed employing the restricted active space state interaction method (RASSI) [20, 21]. This method computes spin–orbit interaction matrix elements in the spin-free eigenstates basis (such as CASSCF or RASSCF wavefunctions) and diagonalizes the resulting matrix in order to produce spin–orbit energy levels and eigenstates. We have used the CASSCF wavefunctions, obtained in the very same manner as in the previous section, as the spin-free basis. However, the diagonal elements of the resulting Hamiltonian matrix were replaced by MRCI energies of the given states, which were computed in the first step. Using this approach, one can correct somewhat inaccurate CASSCF spacing of the energy levels due to the lack of dynamic correlation.

The SO calculations were made for ^{5}D,^{5}F,^{3}D and ^{5}P states using the ANO–RCC basis set in the large contraction, what leads to 16 spin–orbit states (one $J = 0$, three $J = 1$, four $J = 2$, four $J = 3$, three $J = 4$, and one $J = 5$).

3 Results

The spin-free CI + ACPF DKH calculations of the eight lowest even electronic terms of the Fe atom in different contractions of the ANO–RCC basis set are reported in Table 1. As going from the vDZP to the large contraction, the root mean square deviation (RMSD) from experiment gradually diminished. The relative errors in respect of experiment calculated in the large contraction are from 1 to 3%. The exception is the a^{3}P2 and b^{3}F2 term with the error of 7 and 5%, respectively. These two terms exhibit strong coupling with other states. The leading percentage of the a^{3}P term is 55% and in the case of b^{3}F2, it is 71% [10]. Based on the data of Table 1, we believe that the ANO–RCC basis set in the large contraction is suitable for the present study.

Table 1 CI + ACPF DKH calculations of the lowest even electronic terms of the Fe atom

Configur.	Term	vDZP[a]	vTZP[b]	vQZP[c]	large[d]	Expt[e]
$3d^64s^2$	a^{5}D	0	0	0	0	0
$3d^7(^4F)4s$	a^{5}F	8,450	7,129	6,899	7,119	7,057
$3d^7(^4F)4s$	a^{3}F	14,007	12,508	12,283	12,392	12,004
$3d^7(^4F)4s$	a^{5}P	20,549	17,402	17,563	17,871	17,282
$3d^64s^2$	a^{3}P2	21,035	20,438	20,074	19,858	18,551
$3d^64s^2$	a^{3}H	21,054	20,381	19,907	19,649	19,173
$3d^64s^2$	b^{3}F2	22,899	22,213	21,746	21,471	20,411
$3d^7(^2G)4s$	a^{3}G	24,305	22,677	22,107	22,107	21,546
RMSD[f]		2,240	1,108	801	696	0

The ANO–RCC basis sets study. All values in cm^{-1}

[a] The ANO–RCC–vDZP basis set has the [5*s*4*p*2*d*1*f*] contraction, Refs. [19, 26]

[b] The ANO–RCC–vTZP basis set has the [6*s*5*p*3*d*2*f*1*g*] contraction, Refs. [19, 26]

[c] The ANO–RCC–vQZP basis set has the [7*s*6*p*4*d*3*f*2*g*1*h*] contraction, Refs. [19, 26]

[d] The ANO–RCC–large basis set has the [10*s*9*p*8*d*6*f*4*g*2*h*] contraction, Ref. [19]

[e] The spin-average value of the term based on experimental atomic energy levels, Ref. [10]

[f] The root mean square deviation from experiment

Data in Table 2 reveal that upon considering relativistic effects at the basic level of the spin-free DKH method, the agreement between the theoretical CI + ACPF level and experimental excitation energies for all, but the a^{3}P2 term is significantly improved. This is transparently visualized for the transition from the a^{5}D states to the a^{5}F states in Fig. 1, calculated in the vQZP contraction of the ANO–RCC basis set. These results confirm the findings of previous calculations [9, 11, 12] about the importance of relativistic effects even in relatively light element as is iron. With the DKH method for scalar relativistic effects and improved basis sets is the agreement of calculated and experimental EE for this transition much better than before.

Considering also other states, a closer look at the results in Table 2 immediately reveals that there are two different sets of relativistic contributions to excitation energies. For excitations from the ground a^{5}D [Ar]$3d^64s^2$ term to the a^{5}F term and any other terms having the [Ar]$3d^74s^1$ electronic configuration, the relativistic contribution to EE is uniformly large and positive, lying in the interval of about 1,500–2,100 cm^{-1}. For excitations from the ground state to states having the same electronic configuration, [Ar]$3d^64s^2$ is the spin-free relativistic contribution much smaller, less than 400 cm^{-1}. This general picture can be qualitatively understood already considering the model of independent electrons. Relativistic shifts of 3*d* and 4*s* orbitals with respect to nonrelativistic HF orbital energies are schematically drawn in Fig. 2. The relativistic *destabilization* of $3d^6$ orbital configuration is partly compensated by the relativistic stabilization of the $4s^2$ shell. Forgetting for a while the mutual interplay of the electron correlation and relativistic effects, analogous shifts are expected in all states having the [Ar]$3d^64s^2$ electronic configuration. In comparison with the [Ar]$3d^64s^2$ states, there are more *destabilized* $3d^7$ and less *stabilized* $4s^1$ electrons in states characterized by the [Ar]$3d^74s^1$ electronic structure. Therefore, scalar relativistic effects destabilize the energy of [Ar]$3d^74s^1$ states more than energies of the [Ar]$3d^64s^2$ states, and the energy gap and corresponding EEs for transitions between these states are relativistically enhanced.

In Table 3, we present CI + ACPF DKH RASSI calculations of electronic levels for the four lowest electronic terms of the Fe atom, using the large basis set contraction of the ANO–RCC basis set. Our results are compared with calculations of Dzuba and Flambaum [22], who used the

Table 2 Nonrelativistic (NR) and Douglas–Kroll–Hess (REL) calculations of the lowest even electronic terms of the Fe atom

Configur.	Term	NR	REL		Δ^{d}_{rel}	Δ^{e}_{expt}	VMC[f]	Expt[g]
		CI + ACPF[a]	CI + Dav[b]	CI + ACPF[c]				
$3d^64s^2$	a^{5}D	0	0	0	0	0	0	0
$3d^7(^4F)4s$	a^{5}F	5,071	7,036	6,899	1,828	−158	5,710	7,057
$3d^7(^4F)4s$	a^{3}F	10,154	12,354	12,283	2,129	279	9,660	12,004
$3d^7(^4F)4s$	a^{5}P	15,667	17,425	17,563	1,895	281	18,000	17,282
$3d^64s^2$ [h]	a^{3}P2	19,794	20,023	20,074	280	1,523	21,700	18,551
$3d^64s^2$	a^{3}H	20,295	19,908	19,907	−388	734	18,400	19,173
$3d^64s^2$ [h]	b^{3}F2	22,000	21,709	21,746	−254	1,335	19,300	20,411
$3d^7(^2G)4s$	a^{3}G	20,579	22,243	22,107	1,527	561	19,100	21,546

All values in cm^{-1}

[a] Calculations using the ANO–L–vQZP basis that has the [$7s6p4d3f2g$] contraction, Refs. [18, 26]

[b] Calculations using the ANO–RCC–vQZP basis that has the [$7s6p4d3f2g1h$] contraction, Refs. [19, 26]

[c] Calculations using the ANO–RCC–vQZP basis that has the [$7s6p4d3f2g1h$] contraction, Refs. [19, 26]

[d] The difference between REL CI + ACPF and NR CI+ACPF values

[e] The difference between REL CI + ACPF and experimental values

[f] Variational Monte Carlo calculations with a Jastrow factor, Ref. [24]. The values in the original paper are presented in mHartree in two decimal figures with an error varying from 3 to 4 m Hartree, what represent from 660 to 880 cm^{-1}

[g] The spin-average value of the term based on experimental atomic energy levels, Ref. [10]

[h] NIST ASD tables present very strong coupling with other term, Ref. [10]

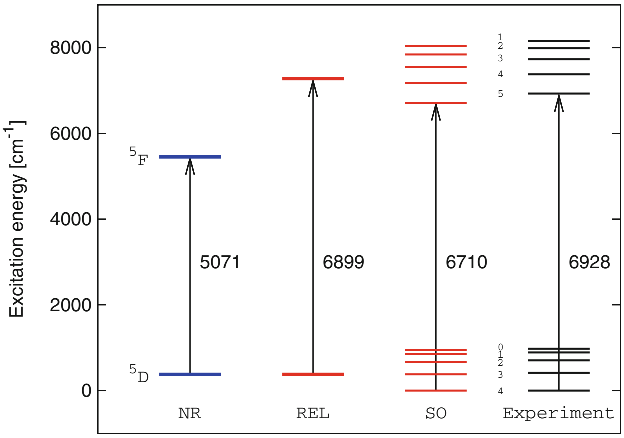

Fig. 1 Comparison of calculated nonrelativistic, spin-free relativistic, spin–orbit relativistic and experimental values of excitations between the two lowest electronic terms of the Fe atom. Calculations using the ANO–L–vQZP basis set

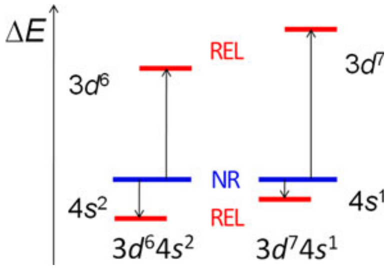

Fig. 2 Schematic relativistic shifts in orbital energies of the $3d^{64}s^2$ and $3d^{74}s^1$ configuration of Fe

Dirac–Hartree–Fock and configuration interaction techniques combined with some semiempirical fitting. Agreement of our values with experimental ones [10] is reasonably good and undoubtedly better than of Dzuba and Flambaum [22], particularly for higher electronic terms.

The differences between our results and the experimental data are significantly smaller for the values of spin–orbit splitting than absolute level of J-states. This is certainly caused by inaccuracies in MRCI calculations. One might expect improvement of these results with the employment of more sophisticated electron correlation method, such as MR–CCSD, especially for higher excited states. However, the calculations would be much more computationally demanding.

The largest error of all considered states is observed in the a^{5}P spin-free term, which has three higher electronic terms (a^{3}P2, z^{7}D°, a^{3}H) placed within 2,000 cm^{-1} above [10]. Such close-lying levels can strongly interact and should be included in the RASSI calculation in order to improve the description of the a^{5}P term. However, the z^{7}D° term with its [Ar]$3d^64s4p$ configuration requires a larger active space, at least $4s3d4p$, which leads again to significantly more demanding calculations. For the remaining group 8 elements, Ru and Os, these 'larger space'

Table 3 CI + ACPF DKH RASSI calculations of electronic levels, level splittings, and term root mean square deviations (RMSD) from experiment for the four lowest electronic terms of the Fe atom

Configur.	Term	J	This work[a]		Dzuba and Flambaum[b]		Expt[c]	
			Level	Split	Level	Split	Level	Split
$3d^64s^2$	a^5D	4	0		0		0	
		3	378	378	464	464	416	416
		2	661	283	790	326	704	288
		1	850	189	1,000	210	888	184
		0	945	94	1,103	103	978	90
RMSD			34	17	87	30	0	0
$3d^7(^4F)4s$	a^5F	5	6,931	5,986	6,862	5,759	6,928	5,950
		4	7,394	463	7,374	512	7,377	448
		3	7,772	378	7,779	405	7,728	351
		2	8,060	287	8,078	299	7,986	258
		1	8,253	193	8,275	197	8,155	169
RMSD			59	27	77	96	0	0
$3d^7(^4F)4s$	a^3F	4	12,315	4,063	13,040	4,765	11,976	3,822
		3	12,933	618	13,702	662	12,561	585
		2	13,393	460	14,171	469	12,969	408
RMSD			380	144	1,137	548	0	0
$3d^7(^4F)4s$	a^5P	3	18,060	4,667			17,550	4,582
		2	18,343	283			17,727	177
		1	18,532	189			17,927	200
RMSD			579	79			0	0

All values in cm^{-1}

[a] Using the large contraction of the ANO–RCC basis set

[b] Ref. [22]

[c] Ref. [10]

calculations will be an absolute necessity. We are planning to calculate the missing terms of the iron atom in the continuation of this work as well.

4 Summary

The pattern of energy states of the iron atom is pretty much relativistic. Even at the level of the scalar relativistic CI + CPF, DKH theory is the relativistic contribution to the excitation energy from the ground a^5D $[Ar]3d^64s^2$ term to the a^5F $[Ar]3d^74s^1$ term as large as $1,828\,\mathrm{cm}^{-1}$ which represents 26.5% of the final excitation energy. Scalar relativistic contributions to all excitation energies from the ground state to any excited state having the $[Ar]3d^74s^1$ electronic structure are similar, around 2,000 cm^{-1}. This feature can be qualitatively understood already at the orbital level by considering the energy stabilization of $4s$ orbitals and destabilization of $3d$ orbitals. Consequently, excitation energies from the ground state to terms having the $3d^74s^1$ valence electronic structure are relativistically enhanced. Analogous considerations allow explaining our result that excitation energies from the ground state to terms having the same $3d^64s^2$ valence electronic structure are affected by scalar relativistic effects very little. Our excitation energy from the ground a^5D_4 state to the a^5F_5 state is 6,931 cm^{-1} and agrees excellently with the experimental value of 6,928 cm^{-1}. Altogether, electronic levels and level splittings calculated by the CI + ACPF DKH RASSI method agree with experimental data reasonably well. The root mean square deviations from experiment for the ground state are quite small (34 and 17 cm^{-1} for electronic levels and level splitting, respectively). These deviations are larger for the next three terms. Accurate calculations of energy levels of higher excited states require larger active space to properly treat strong interactions between close-lying levels.

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References

1. Pyykkö P, Desclaux JP (1979) Accounts Chem Res 12:276
2. Pyykkö P (1988) Chem Rev 88:563
3. Pyykkö P (1997) Chem Rev 97:597
4. Pyykkö P (2004) Angew Chem-Int Edit 43:4412
5. Reiher M, Wolf A (2009) Relativistic quantum chemistry: the fundamental theory of molecular science. Wiley-VCH, Weinheim
6. Schwerdtfeger, P (eds) (2002) Relativistic electronic structure theory. Part 1. Fundamentals. Elsevier, Amsterdam
7. Schwerdtfeger, P (eds) (2004) Relativistic electronic structure theory. Part 2. Applications. Elsevier, Amsterdam
8. Iliaš M, Kellö V, Urban M (2010) Acta Phys Slovaca 60:259
9. Urban M, Watts JD, Bartlett RJ (1994) Int J Quantum Chem 52:211
10. Ralchenko Y, Kramida AE, Reader J, NIST ASD Team (2010) NIST Atomic Spectra Database (ver. 4.0.0) [Online]. Available: http://physics.nist.gov/asd, National Institute of Standards and Technology, Gaithersburg
11. Martin RL, Hay PJ (1981) J Chem Phys 75:4539
12. Bauschlicher CW (1987) J Chem Phys 86:5591
13. Balabanov NB, Peterson KA (2005) J Chem Phys 123:064107
14. Balabanov NB, Peterson KA (2006) J Chem Phys 125:074110
15. Douglas M, Kroll NM (1974) Ann Phys (NY) 82:89
16. Hess BA (1985) Phys Rev A 32:756
17. Hess BA (1986) Phys Rev A 33:3742
18. Pou–Amérigo R, Merchán M, Nebotgil I, Widmark PO, Roos BO (1995) Theor Chim Acta 92:149
19. Roos BO, Lindh R, Malmqvist PA, Veryazov V, Widmark PO (2005) J Phys Chem A 109:6575

20. Malmqvist PA, Roos BO, Schimmelpfennig B (2002) Chem Phys Lett 357:230
21. Roos BO, Malmqvist PA (2004) Phys Chem Chem Phys 6:2919
22. Dzuba VA, Flambaum VV (2008) Phys Rev A 77:012514
23. Buendia E, Gálvez FJ, Sarsa A (2006) J Chem Phys 124:154101
24. Buendia E, Gálvez FJ, Maldonado P, Sarsa A (2010) J Phys Chem A 114:1953
25. Dzuba VA, Flambaum VV, Webb JK (1999) Phys Rev Lett 82:888
26. Aquilante F, De Vico L, Ferre N, Ghigo G, Malmqvist PA, Neogrády P, Pedersen TB, Pitoňák M, Reiher M, Roos BO, Serrano–Andrés L, Urban M, Veryazov V, Lindh R (2010) J Comput Chem 31:224
27. Langhoff SR, Davidson ER (1974) Int J Quantum Chem 8:61
28. Gdanitz RJ, Ahlrichs R (1988) Chem Phys Lett 143:413