

Aspects of spin-orbit effects in compounds containing heavy elements

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Abstract This perspective article discusses some widely-known and some less-known consequences of spin-orbit effects in inorganic chemistry, and provides a brief outline of the theoretical methods currently in use, along with a discussion of recent developments and selected applications. This is of critical importance in the interpretation of the electronic delocalization, optical and magnetic properties and Jahn–Teller effects of compounds containing heavy elements.

Keywords Spin-orbit · Relativistic effects · Jahn-Teller · Aromaticity · Double group · Heavy element

1 Introduction

Relativistic effects, though minor in light atoms, increase approximately quadratic with the atomic number Z down a column in the periodic table [1]. The considerable number of discrepancies between the classical quantum mechanics and experiment is due to the neglect of relativistic effects. For heavy atom species, it becomes necessary to discard the Schrödinger equation in favor of the Dirac equation. Construction of an effective many-body Hamiltonian that accurately accounts for both relativistic and electron correlation effects in many-electron systems is a challenge. It is only in the past 20–25 years that relativistic quantum chemistry has emerged as a field of research in its

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own right, and it seems certain that relativistic many-electron calculations of molecular properties will assume increasing importance in the years ahead as relativistic quantum chemistry finds a wider range of applications.

Quantum mechanics and the theory of relativity are two of the most important scientific developments of the twentieth century. Most of the structure of non-relativistic (NR) quantum mechanics was put into place between 1925 and 1927, followed a few years later by Dirac's incorporation of special relativity [2–4]. Indeed it was not until the 1970s that the chemical consequences of relativity in molecules were envisioned and special computational algorithms, that solve the Dirac equation were created [5, 6]. Since then, there has been extensive investigations of the role of relativity in chemistry [1, 7–11]. The contraction and stabilization of *s* and *p* shells, and the expansion and destabilization of *d* and *f* shells, termed as *direct* and *indirect* relativistic effects respectively, were the starting points for qualitative and quantitative investigations. Well-known examples include: the relativistic contraction of bond lengths [12], the color of gold [13], change of the chemical bond due to np_σ towards $np_{1/2}$ bonding along a series of diatomic hydrides [14, 15], prediction of superheavy elements and molecules [16–18]. The explanation why mercury is liquid at room temperature, has been ascribed to strong relativistic effects [7–9], but the first evidence that this explanation is correct has only recently been reported by Schwerdtfeger, Calvo et al., by performing state-of-the-art quantum chemical calculations [19].

Quantum mechanical computations using the Dirac equation involve four-component operators that are computationally very expensive [20]. Thus, it is not a coincidence that the emergence of the field parallels the improvement of computer technology and also the development of new computational quantum chemistry methods, for it is only through the latter technique that we can directly compare NR atoms and molecules with their relativistic analogues.

Apart from the well-known *direct* and *indirect* relativistic effects, one of the principal consequences of the Dirac equation for chemistry stems from its prediction of the electron spin. When an electron is part of an atom, the magnetic moment associated with its intrinsic spin angular momentum couples with the magnetic field generated by its orbital motion. This spin-orbit (SO) coupling results in states that are characterized by the half-integral total angular momentum quantum number, j , as a result of the combination of integral orbital angular momentum quantum number ($l = 0, 1, 2, 3, \dots$) with non-integral spin angular momentum quantum number ($s = \pm 1/2$). Except for *s* orbitals, for which there is no orbital angular momentum ($l = 0$), the SO interaction splits a shell of given l into sub-shells with total angular momentum $j = l - 1/2$ and $j = l + 1/2$. The factors which govern the magnitude of this SO splitting in many-electron atoms are complicated but, in general, the SO coupling increases significantly with increasing nuclear charge and, for a given primary quantum shell, decreases in the order $p > d > f$ [20]. In the relativistic framework, the angular momentum l and spin s quantum numbers are not constants of motion; only the total angular momentum quantum number $j = l + s$ is conserved, hence spin and spatial symmetry cannot be treated separately. This has profound consequences for the description of the symmetry of molecular systems. For half-integral values of j the wave functions for Fermions (spinors) are not periodic in 2π and but rather in 4π (actually a rotation by 2π has the effect of changing the sign of the spinors). This need to rotate by 4 to

generate the identity operation led to the invention by Hans Bethe of the theory of *double groups* [21]. With this new identity operation, every *double group* contains the double of elements of the *single group* but not necessarily the double of irreducible representations (irreps) [22,23], and these *extra irreps* are given by Opechowski's rules [24]. It is customary to use Bethe's Γ notation for double groups instead of the standard Mulliken's notation for single-group irreps [25,26].

All integral angular momentum states [e.g. NR, spatial molecular orbitals (MOs)] have symmetry properties which span one or more of the familiar *single-group irreps*. On the other hand, all states characterized by non-integral angular momentum values (e.g. relativistic spin orbitals) have symmetry properties which span one or more of the *extra irreps* of the double group [20]. The group theoretical relationship between NR spatial MOs and their relativistic spin-orbital counterparts may be obtained by decomposing the reducible representation created by the direct product of the *single-group irreps* with that of electron spin, Γ_{spin}^* . For example, if ψ correspond to an occupied MO then the direct product of irreps

$$\Gamma^\psi \otimes \Gamma_{spin}^* = \Gamma_1^* \oplus \Gamma_2^* + \dots$$

decomposes the single-group irrep Γ^ψ into the double-group irreps (extra irreps) $\Gamma_1^*, \Gamma_2^*, \dots$. In fact, it is frequently found that SO coupling lifts the degeneracy of *single-group irreps*, generating additional energy levels. This is of critical importance in the interpretation of the electronic delocalization [27,28], optical and magnetic properties [29,30] and Jahn–Teller effects [31] of compounds containing heavy elements.

There are dramatic cases in the literature. For example in the chloriodomethane cation, CH_2ClI^+ , the experimental and theoretical findings showed a dramatic discrepancy when the SO interaction is neglected [32]. In fact, SO was crucial for the identification of the structure and vibrational frequencies of the correct ground state of this open-shell molecule. In contrast, it was also shown that for the neutral molecule the neglect of the SO interaction on the vibrational frequencies is not significant. Also the inclusion of super-heavy elements can have dramatic effects on atomization energies. In the tetrahedral super-heavy hassium tetroxide (HsO_4) the predicted relativistic atomization energy increases by about 225 % from the corresponding NR value [33]. In the lighter analogue (OsO_4) this increase can be about 185 %.

The goal of this work is to present a short description of some aspects of the SO interaction that have been overlooked by more extensive reviews. We will focus mainly on first-order SO effects, although higher-order SO effects can also be important (see Ch. IV. A. 8. of reference [34]).

2 Chemical shifts and aromaticity

Frequently the phenomenon of electronic delocalization is used for understanding the unusual stability of planar cyclic molecules that exhibit delocalized π -bonds. Initially, aromaticity was developed only for organic compounds, but today this concept has been extended to a large number of compounds, such as, inorganic and organometallic

complexes as well as molecular metal clusters by a combination of photo-electron spectroscopy and theoretical calculations. The relativistic density functional theory (DFT) calculations of the electronic structure and nucleus-independent chemical shifts (NICS) [35] values of the Re_3Cl_9 , Re_3Br_9 , $\text{Re}_3\text{Cl}_9^{2-}$ and $\text{Re}_3\text{Br}_9^{2-}$ clusters including scalar and SO relativistic effects have shown that these clusters exhibit aromaticity which is affected by the SO coupling [27, 28, 36]. In order to explain the SO influence, it is useful to rationalize it in terms of the atomic orbitals of rhenium (Re). The highest molecular orbitals (HOMOs) in these clusters are mainly metallic with significant $5d$ character, and the SO coupling splits the $\text{Re}(5d)$ levels into the $5d_{3/2}$ and $5d_{5/2}$ levels which help to explain the SO influence on the NICS values.

Early experimental evidence that NMR chemical shifts are strongly affected by SO effects, can be found in reference [37] where Japanese workers found important effects in proton NMR chemical shifts of mono-substituted benzene (halobenzenes). From the theoretical point of view, SO corrections to NMR shielding constants in heavy systems has been reported by a number of studies [38–42].

3 Magnetically induced current densities

Magnetically induced current densities are intimately related with the concept of aromaticity. The magnetically induced current density is obtained through linear response of the Hartree–Fock or Kohn–Sham determinant to a perturbing magnetic field, applied perpendicular to the molecular plane. Current density plots and integrated current densities (current strengths) are thereby used as a criterion for aromaticity or electron delocalization. Current strengths should be affected by strong relativistic effects in heavy systems. In fact, magnetically induced current densities turned out to be a better probe for aromaticity than the NICS method, especially when f electrons are involved [43].

Both induced current densities and NICS values can be described in terms of the accessibility of low-lying excited electronic states. The idea is that the magnetic property can be divided into a paramagnetic and a diamagnetic part, and the nature of the excitation is determined by symmetry selection rules [44, 45].

Corminboeuf et al. [46] found that the contributions to the paramagnetic term of the NICS values are determined by rotationally-allowed transitions. If ψ_i and ψ_a correspond to occupied and unoccupied MOs respectively then the transition is rotationally-allowed if the direct product of irreps

$$\Gamma^{\psi_i} \otimes \Gamma^{\psi_a} \otimes \Gamma^{R_z}$$

contains the totally symmetric representation of the molecular point group. Another factor that affects the magnitude of NICS values is the occupied-to-unoccupied orbital energy difference term $\Delta E_{occ-unocc} = \varepsilon_i - \varepsilon_a$, because the paramagnetic part is a sum-over-states where the terms $1/\Delta E_{occ-unocc}$ appear as amplitudes (see, for instance, Eq. (1) of Ref. [46]). This means that the major contributions to the paramagnetic term should come from the HOMO-LUMO rotational transition and from a few high-lying orbital pairs. But as stated in the introduction, SO can lift the degeneracy

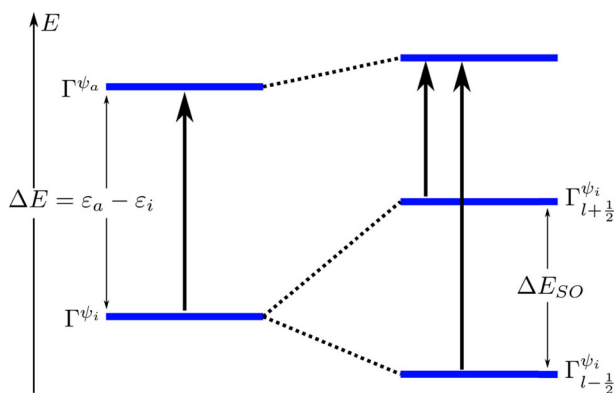


Fig. 1 The ψ_i and ψ_a correspond to occupied and unoccupied MOs respectively. The SO coupling can affect the magnitude of the allowed transitions, and additional excitations can be allowed due to degeneracy lifting. The ψ_i energy level splits into two levels with total angular momentum quantum numbers $j = \pm 1/2$. Furthermore the allowed transitions can change symmetry thus affecting significantly the paramagnetic/diamagnetic contributions to the magnetic property

of *single-group irreps*, generating additional energy levels which now have different symmetry (double group), thus modifying the orbital contributions to the NICS value. Figure 1 shows a general example where an excitation energy can vary going from *single group* symmetry to *double group* symmetry. Furthermore the *single-group* rotationally-allowed transition can be forbidden in the *double-group* framework thus affecting significantly the paramagnetic contribution.

4 The Zeeman g-tensor

For compounds containing light elements, the g-tensor anisotropy can be treated perturbatively, *i.e.* as a higher-order spin-orbit effect. In contrast, it is now well documented that SO effects are much larger than crystal field effects in lanthanide and actinide complexes, and for these cases we have to solve the Dirac equation because the Hamiltonian needed requires both the large and small components of the molecular wavefunction to describe correctly the magnetic interactions.

For example, while NR theories predicts only two absorption bands for the ions UF_6^- and PaCl_6^{2-} , the relativistic theory predicts four absorption bands in excellent agreement with experiment [29,30].

The magnetic properties of radical complexes containing actinide ions are often complicated by orbital contributions to the Zeeman tensor arising from SO mixings with low lying excited states, because their observed molecular g-tensors are significantly shifted from the spin-only value of $g_e = 2.0023$. Since these contributions from electronic orbital motion are neither isotropic nor traceless, one cannot make a simple decomposition of the observed hyperfine tensors into isotropic and anisotropic parts. Moreover, in the absence of SO mixing, a $S = 1/2$ complex system will exhibit resonance at the spin-only value. However, in the presence of SO coupling the changes are dramatic. In effect, the UF_6^- and PaCl_6^{2-} ions which are $S = 1/2$ magnetic systems,

Table 1 Isotropic Zeeman tensors

	Complex	EPR parameter	NR	REL	Exp.
^a $\Delta g(\text{Calc.}) \approx g_{\text{iso,REL}} - g_{\text{iso,NR}}$; $\Delta g(\text{Exp.}) \approx g_{\text{iso}} - g_{\text{e}}$	PaCl_6^{2-}	g_{iso}	+2.026	−1.208	−1.142 ^b
		Δg_{iso}	−3.234 ^a		−3.144 ^{a,b}
^b Reference [47], ^c Reference [48]	UF_6^-	g_{iso}	+1.926	−0.952	−0.78 ± 0.10 ^c
		Δg_{iso}	−2.878 ^a		−2.78 ± 0.10 ^{a,c}

are characterized by negative isotropic Zeeman tensors quite far from the NR limit of g_{e} (observe the dramatic change in sign in Table 1) [29,30]. This type of calculations are specially challenging for computational codes for it is strongly advisable to solve the full Dirac equation.

5 Jahn–Teller distortions

About 55 years ago the synthesis of platinum hexafluoride (PtF_6) was first reported, thus extending the number of known third-row transition-metal series ($5d$) that form the hexafluorides (WF_6 , ReF_6 , OsF_6 and IrF_6) [49]. It is well documented, in inorganic chemistry text books, that high-spin d^4 octahedral complexes are energetically unstable and experience deformation from octahedral geometry due to the Jahn–Teller effect [50,51]. The structure and ground state of PtF_6 has been a longstanding problem for theoretical chemists. Indeed all theoretical studies, avoided the SO coupling, and reported a distorted octahedral molecular structure with a triplet ground state.

Platinum hexafluoride is unique; it is the only platinum compound with the formal oxidation state VI and in spite of its d^4 electronic configuration it is strictly octahedral, in contrast to the hexafluoride complexes containing Re, Os, and Ir. The electronic structure of octahedral complexes can be described qualitatively in terms of crystal field diagrams. Speaking in NR terms, the t_{2g} orbital (Fig.2-left) houses four unevenly distributed (not equally populated) electrons, which means that the complex should undergo a Jahn–Teller (tetragonal) distortion, yielding a D_{4h} symmetry. This complex has been a challenge for computational quantum chemistry codes. In effect, all previously published NR and scalar relativistic (SO switched off) structure calculations of PtF_6 predict a paramagnetic distorted octahedral molecule with a triplet ground state. However the full symmetry of PtF_6 must be analyzed in terms of double-group theory where the t_{2g} (γ_5^+) energy level (Fig. 2-left) splits into two levels, γ_8^+ and γ_7^+ . In this modified crystal field (Fig. 2-right), the γ_8^+ spinor can house four electrons, hence the system is (qualitatively) a *closed-shell*, with four electrons evenly distributed. Under this condition the system cannot undergo a Jahn–Teller distortion, and it will remain in octahedral geometry (O_h symmetry).

Relativistic DFT and Dirac–Hartree–Fock calculations of the electronic structure, including scalar and SO relativistic effects method also predicts a perfectly octahedral molecule with a closed-shell ground state [31,52], which is in accordance with NMR [53] and Raman [54] experiments. The four-component calculations [31,52] also showed that when the SO interaction is switched off, the molecule distorts toward D_{4h} symmetry, implying that the Jahn–Teller effect is canceled by the SO interaction.

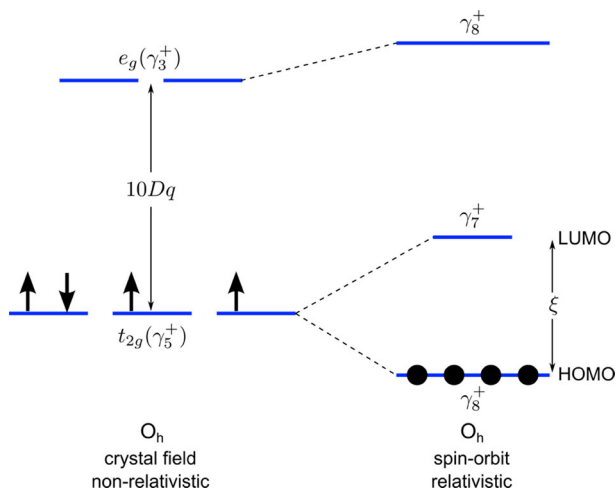


Fig. 2 The d^4 configuration of PtF_6 under the influence of an octahedral crystal field. Both, Mulliken's and Bethe's Γ notations are used for energy levels. Notice that in the NR case *up* and *down* arrows have been used to indicate spin. In the relativistic case spin is not a "good quantum number", hence spin is indicated by *circles*

This interesting interplay, between a large SO interaction and the ground state electronic structure of a molecule has also been reported by other authors [55, 56]. From the theoretical point of view, Poluyanov and Domcke have derived explicit Hamiltonian matrices for electronic states in tetrahedral and cubic systems [57–59]. In reference [59] they show that for a single d -electron in an octahedral crystal environment the t_{2g} mode becomes Jahn–Teller-active through the SO operator.

The influence of the SO interaction in Jahn–Teller effects has also been found in molecules containing superheavy elements. See for instance the works of Nash and Bursten [60–62] where they report that the influence of SO effects on bonding is so great as to challenge the VSEPR theory. Metal clusters are also affected. For example, SO coupling favors a Jahn–Teller distortion in the Pt_3 cluster, to an isosceles triangle [63].

More examples about the competition between SO coupling and the Jahn–Teller effect can be found in section 4.6 of reference [11].

6 Conclusions

This article attempts to present to chemistry students and teachers some chemically interesting results of relativistic quantum chemistry in inorganic systems. Apart from the well-known relativistic effects in chemistry, nicely described by Pyykkö [9–11], there are other effects that have been overlooked. Here we described relativistic effects affecting optical, magnetic and aromatic properties on molecules containing heavy atoms. We also explained the role of SO coupling by switching off the Jahn–Teller effect in platinum hexafluoride. We strongly believe that the Dirac treatment and its

consequences in inorganic chemistry have a definite place in relativistic quantum chemistry.

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