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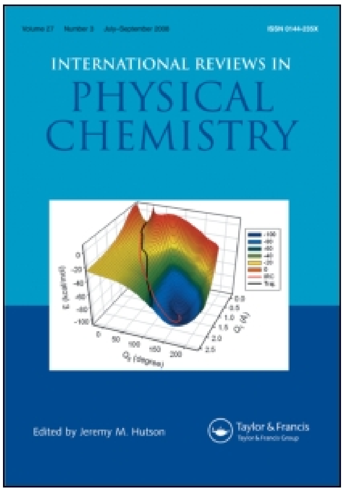

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# Spin-orbit coupling in molecules: Chemistry beyond the adiabatic approximation

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# Spin–orbit coupling in molecules: chemistry beyond the adiabatic approximation

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An extensive introduction to spin–orbit coupling (SOC) is presented, starting from a discussion of the phenomenological operators and general chemical importance of SOC to studies of chemical reactions. Quantitative SOC operators are discussed, and the symmetry properties of the SOC Hamiltonian important for understanding the general features of SOC are summarized. Comparison of the one- and two-electron contributions to SOC is given, followed by a discussion of commonly used approximations for the two-electron part. Applications of SOC to studies using effective and model core potentials have been analysed. The theoretical discussion is illustrated with numerous practical examples, including diatomic molecules (with an emphasis on hydrides) and some examples for polyatomic molecules. The fine structure of the SOC interaction (vibrational dependence) for some diatomic molecules has been elucidated.

## Contents

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## 1. Introduction

The phenomenon of spin–orbit coupling (SOC) arises from the interaction of the intrinsic magnetic moment of an electron with its orbital angular momentum. Every chemist is familiar with the splitting of the sodium D line into two, which originates from the valence electron in an excited p orbital, where the excited p electron with orbital angular momentum $l = 1$ and spin angular momentum $s = 1/2$ couples these two to a total angular momentum of $j = 3/2$ or $j = 1/2$. The two lines in Na are separated by $17\,\mathrm{cm}^{-1}$, so even a crude instrument is capable of detecting the effect of SOC.

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A recent review of SOC by Marian (2001) presents a good summary of the physics of the interaction as well as various methods for its computation. The present review focuses on our own work involving the Breit–Pauli spin–orbit (SO) Hamiltonian, $H^{\mathrm{SO}}$. Langhoff and Kern (1977) present an overview of the derivation of this operator, the spin–spin operator and other terms appearing as a result of Pauli's transformation of the Dirac equation in their review of molecular fine structure. Pyykkö (1978) and Balasubramanian (1997) give similar equations relating $H^{\mathrm{SO}}$ to other relativistic effects. References to alternatives to the Breit–Pauli SO operator included below are intended only as a brief summary and are typically limited to the most recent papers. Any reader with a greater interest in techniques for computing this property may find additional details in Marian's excellent review (2001) or in Marian (1997).

Hess *et al.* (1995) also discuss computational methods for the SO effect and give numerous numerical results. An earlier review (Yarkony 1992) focused on the perturbative use of the Breit–Pauli SO operator for light elements. A review of the use of effective core potential (ECP) operators for SOC exists (Ermler *et al.* 1988), as well as a monograph concerned with SO effects in atoms and diatoms (Richards *et al.* 1981). Ågren *et al.* (1996) review the computation of the influence of SOC on spectral properties.

In lighter elements, where the SOC is weaker than the ordinary electron repulsion terms, Russell–Saunders coupling applies. Conversely *j–j* coupling is appropriate for the heaviest elements. If we consider atoms, this means that lighter elements retain $L$ and $S$ as approximate quantum numbers, each formed from the separate vector sums of $l_i$ and $s_i$ for each individual electron, with the quantized total angular momentum $J$ being the result of the vector sum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$. A typical example is provided by the group 14 $s^2p^2$ elements. The lowest energy $^3P$ term of this configuration splits into three different $J$ levels, $^3P_0$, $^3P_1$ and $^3P_2$, spaced $43\,\mathrm{cm}^{-1}$ apart for C and $223\,\mathrm{cm}^{-1}$ for Si, increasing to $10650\,\mathrm{cm}^{-1}$ for Pb. For Pb, these three $J$ levels remain grouped together as the lowest three levels, but their separation is a significant fraction of the excitation energy to the next term, $^1D_2$, at $21\,457\,\mathrm{cm}^{-1}$.

Thus, while it may make qualitative sense to retain the *L*–*S* notation $^3$P for Pb, it is clear that its SOC is quite large. In the heavy atom limit, it is more accurate to couple $l_i + s_i$ for each electron to $j_i$ and then to construct many-electron states by coupling the $j_i$ to obtain $J$. This is called the *j*–*j* coupling limit and is appropriate in the lower reaches of the periodic table. Tables of atomic spectra (Moore 1949, 1952, 1958) may not even assign $^{2S+1}L_J$ labels giving approximate $L$ and $S$ values for sixth-row atoms, in favour of listing only the precise $J$ quantum number. For example, the experimental $J = 2$, 775.9 cm$^{-1}$ level of Pt is now known (Dyall 1993a) to consist of 40% $^3D_2$ ($d^9s^1$), 38% $^1D_2$ ($d^9s^1$) and 16% $^1D_2$ ($d^8$) character and therefore cannot be regarded as either singlet or triplet.

Let us consider some additional examples of the importance of SOC from a chemical viewpoint. The great increase in strength of the SOC as we descend through the periodic table has implications for whether or not we try to include it in computations and, if so, by what means.

For the most part, SOC is simply ignored for light elements. This is possible because SOC in general is smaller for lighter elements. It is also common for molecules containing light elements to be very well described by singlet, single-configuration wavefunctions, for which symmetry forces SOC to be zero to first order as explained in detail below. However, if chemical reactions involving atoms or other open-shell species are considered then SOC cannot be ignored if accuracy on the order of 1 kcal mol$^{-1}$ is sought after. Even for an atom as light as fluorine, the SO splitting of the ground state is 404.1 cm$^{-1}$ (Moore 1949), and thus ignoring SOC would result in an error of 0.38 kcal mol$^{-1}$ ($^2$P level splits into $^2P_{3/2}$ and $^2P_{1/2}$). It is clear that, in organic systems, SOC is a primary decay process for metastable triplet states, through intersystem crossings (ISCs).

Organic photochemistry (Salem and Rowland 1972, Robb *et al.* 2000) often involves metastable triplet structures, whose only decay mechanisms are both spin forbidden: phosphorescence or non-radiative ISC. ISC rates are highest along the seam of intersection of two potential energy surfaces with different spin multiplicities, with dynamical factors favouring ISC events at the minimum energy crossing (MEX) points (Yarkony 1990). The MEX is the lowest energy point on such a seam, and it serves in some sense as the 'transition state' for ISC. Automated procedures for locating MEX points exist (e.g. Farazdel and Dupuis 1991), and models such as Landau–Zener (Landau 1932, Zener 1932, Nakamura 1987) may be used to compute rates. More sophisticated treatments of ISC rates include the use of Fermi's golden rule or non-adiabatic Rice–Ramsperger–Kassel–Marans (RRKM) calculations, as illustrated by a study of the $T_1$ decay rate in norbornadiene (Harvey *et al.* 2000).

Other organic applications are the stereochemical control exerted by ISC on reactions in Paterno–Buchi radicals (Kutateladze 2001) and inclusion of SO as well as spin–spin coupling effects on the lifetimes of triplet states of *m*-xylylene (Havlas and Michl 1999) and ISC lifetimes in cyclic α,β-enones (Garcia-Exposito *et al.* 2001). There is significant interest in general in the phenomenon known as the heavy atom effect that is the perturbation of SOC in a system due to a heavy atom. This phenomenon manifests itself as the change of lifetimes and reaction rates due to SOC. The effect is classified as external when the heavy atom is not chemically bound to the system, such as solute–solvent types of interactions, pioneered by the work of Kasha (1952), and some more recent work includes the theory of SOC of alkali and noble metals in rare gas matrices due to Pellow and Vala (1989) and a study of CAr

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by Sohlberg and Yarkony (1999). The other type is internal, when a heavy atom resides in a molecule, first theoretically studied by McClure (1949), and more recent work includes the study of the phosphorescence rate in 9,10-anthraquinone haloderivatives by Korol'kova *et al.* (1999) and the study of the inverse heavy atom effect in $HCCH_2Br$ by Havlas and Michl (2002), to name just a few.

Second-row examples are not limited to organic compounds. For instance, the full spectrum of spin-forbidden transitions in $O_2$ has been obtained (Klotz and Peyerimhoff 1986). Inclusion of SOC produces better agreement with experimental intensity patterns in the extensively studied molecular beam reaction $F + H_2$ (Aquilanti *et al.* 2002). Typically, SOCs are a few tens of $cm^{-1}$ for molecules formed from second-row elements, and perturbative treatments are clearly appropriate. In addition, very accurate experiments on small molecules and molecular ions have been performed (e.g. Fedorov *et al.* 1999) that require computation of SOC for an adequate understanding of the spectroscopy. Light atom examples are not limited to organic photochemistry but also included detailed spectroscopic measurements.

For intermediate weight main group elements, SO interactions grow to the order of hundreds to a few thousand $cm^{-1}$ and of course are easily observed spectroscopically. One example of this is the agreement found between experimental measurements and Fermi's golden rule lifetimes in the predissociation of $A\,^3\Pi$ PH by a repulsive $^5\Sigma^-$ state (Fitzpatrick *et al.* 2002). Another example is the computation of lifetimes in excited states of TeF (Rai *et al.* 2001). The energy contribution from SOC is large enough that it must be included in model thermochemistries such as the G2 theory for Ga–Br (Duke 2001), and experimental atomic SOC values are used in the follow-on G3 method (Curtiss *et al.* 1998). Experiments show that the $Cl^*\ ^2P_{1/2}$ level has a large non-adiabatic reactivity in $Cl + H_2$ dynamics (Hanf *et al.* 2001, Dong *et al.* 2001). A Rosen–Zener–Demkov model used for the study of photodissociation of $Cl_2$ reproduces the experimental branching ratio for $^2P_{3/2}$–$^2P_{1/2}$ atoms (Asano and Yabushita 2001). Spectra of SrSH reveal a second-order SOC through an effective $\Pi$ state in this strongly bent molecule (Halfen *et al.* 2001). Finally, inclusion of SOC is found to improve agreement with experimental nuclear magnetic resonance (NMR) shifts in $SnX_4$, $X = Cl$, Br, I, via its effect on the Fermi contact term (Kaneko *et al.* 1996).

Transition metal compounds have a rich set of electronic states owing to unfilled d shells, and therefore SO effects are commonplace. SOC perturbs the potential curves of several states in FeC and has been found to be bond length dependent in two of these (Itono *et al.* 2001). A key step in $H_2$ dissociation on $Pd_4$ clusters is a triplet–singlet transition induced by SOC (German *et al.* 2001). Photoemission spectra in the insulator $Ca_2RuO_4$ show there is a strong SOC in the bands arising from the Ru 4d $t_{2g}$ orbitals (Mizokawa *et al.* 2001). The paradoxical observation of a decrease in reaction rate with increased collision energy between $FeO^+$ and $H_2$ has been explained by invoking an ISC between a sextet and quartet state, with an increased probability when high kinetic energy does not carry the reactants too rapidly past this region of the surface (Danovich and Shaik 1997).

It is of course simple to find additional examples in very heavy elements. Therefore we will give only four examples in addition to the Pt atom already mentioned. Probably the second most familiar manifestation of SOC in chemistry, after the Na D line mentioned above, is the mercury sensitization technique. This is due to the absorption at 253.7 nm by the ground state $^1S_0\ 6s^2$ atom to the $^3P_1\ 6s^16p^1$ level, whose $\Delta J = 1$ transition is dipole allowed. The 'triplet' character of this excited

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state can be transferred to organic compounds via collisions, producing metastable triplet species whose direct optical excitation would have had vanishing intensity. SO effects are found to be influential on both bond distances and dissociation energies in the sixth-row hydrides AH, A = Tl–At, and are very large in their hypothetical seventh-row analogues (Han *et al.* 2000). Splittings in the +3 lanthanide ions have been compared with experiment (Sanoyama *et al.* 1998). The transuranic compound $AmF_4$ has many levels arising from a $5f^5$ atomic configuration, which can be modelled to an accuracy of about $40\,cm^{-1}$ up to $19\,000\,cm^{-1}$ (Liu *et al.* 1994).

Entering the topic 'spin–orbit coupling' into Chemical Abstracts in 2002 produces almost 10 000 references, so clearly the examples shown above only scratch the surface of work in this area. An additional list of examples from light to heavy elements has been given elsewhere (Koseki *et al.* 2001a). Danovich *et al.* (1998) also give a large number of references to important SOC effects in chemistry. The increasing interest in SO effects in chemistry is responsible for development of methods for the computation of this property as well as their use in chemical problems. This review is therefore divided into two main parts, one concerned with theoretical methods for the treatment of SOC and one on applications. The emphasis is on our own work in this field. Although the theoretical section contains some review of alternative methods, this review is not intended to be exhaustive. Some concluding remarks end the review.

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## 2. Theoretical aspects of spin–orbit coupling

### 2.1. *A survey of methods for the computation of spin–orbit coupling*

Having established that SOC is relevant in chemistry, even for light elements, we now turn to methods for its calculation. Since *j–j* coupling is appropriate in the heavy atom limit, it is clear that use of the four-component Dirac equation is ideal (Quinney *et al.* 1999). The Dirac equation for a hydrogenic atom yields four component spinors, with $j = l + s = l \pm 1/2$ distinguishing between the two ($\alpha$ and $\beta$) 'large' components and the two ($\alpha$ and $\beta$) 'small' components. One four-component equation, in other words, is a set of four coupled one-component equations, and $\alpha$ and $\beta$ spins are explicitly coupled, and thus the one-electron Dirac equation already includes the SOC effect. Addition of the $1/r_{ij}$ electron repulsion terms gives the Dirac–Coulomb equation, to which one may add the Breit interactions (Breit 1929) or the Gaunt approximation to these (Gaunt 1929), encompassing the two-electron part of SOC. Programs capable of molecular four-component Dirac–Coulomb or Dirac–Coulomb–Breit calculations are becoming increasingly common, and recently Visscher (2002) has given a summary of the progress and prospects for these. Recent implementations of four-component calculations include Dirac–Hartree–Fock (Visscher *et al.* 1989, Matsuoka 1992, Dyall 1993b, Saue *et al.* 1997, Pernpointner *et al.* 2000, Grant and Quiney 2000, de Jong and Visscher 2002, Yanai *et al.* 2002, Nakajima *et al.* 2002), as well as extensions to correlation methods including density functional theory (Liu *et al.* 1997, Yanai *et al.* 2001, Saue and Helgaker 2002), perturbation theory (Dyall 1994, Laerdahl *et al.* 1997, Laerdahl *et al.* 1998), multiconfigurational methods (Jensen *et al.* 1996, Fleig *et al.* 1997, Vilkas *et al.* 1998, Ishikawa and Vilkas 2001) and coupled cluster theory (Eliav *et al.* 1994, Visscher *et al.* 1995, Visscher *et al.* 1996, Visscher *et al.* 2001), together with properties such as NMR (Ishikawa *et al.* 1998).

The Gaunt or Breit term is frequently treated as a perturbation but may be treated variationally.

There are four equations in the one-particle Dirac equation, containing as its unknowns four spinors, which collectively form a four-component wavefunction. Solution of these equations also provides the energy of the system. The four components consist of two 'large' and two 'small' components, corresponding to the electron and the positron; the amplitude of the former is usually much greater than that of the latter. For highly relativistic core electrons, the 'small' components actually have appreciable magnitude (in the non-relativistic limit $\Psi_{\text{small}} = (1/2mc)(\sigma \cdot \hat{\mathbf{p}})\Psi_{\text{large}}$, where $2mc$ in atomic units is approximately equal to 274). Both valence 'large' spinors resemble in shape the non-relativistic orbital, while the 'small' components have their maximum amplitude at much smaller radii. In atoms, there is a quantum number that distinguishes between the two different 'large' and two different 'small' components. This quantum number may be related to the quantum number $j$, which is the vector sum of the usual orbital angular momentum $l$ and spin angular momentum $s = 1/2$, by $j = l + 1/2$ or $j = l - 1/2$. Thus the differences between each pair of components are seen to be a consequence of SOC. Illustrations of the radial shapes of the four spinors of the valence atomic orbitals of Pb (Lee *et al.* 1977) and U (Kahn *et al.* 1978) may be helpful to a reader unfamiliar with four-component wavefunctions. Standard physics texts containing expositions of the Dirac and other relativistic equations include Bethe and Salpeter (1957), Messiah (1961), Bethe and Jackiw (1964) and Sakurai (1967), each of which has been reprinted frequently.

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It is possible to manipulate the four equations to eliminate the two small component spinors corresponding to positrons, producing a two-component equation (e.g. van Lenthe *et al.* 1996). One may also eliminate the spin dependence of the Hamiltonian, making it spin free, thereby eliminating a third component and producing a single-component equation. There has been a great deal of work on these eliminations, with Foldy–Wouthuysen (Foldy and Wouthuysen 1950) and Douglas–Kroll (Douglas and Kroll 1974, Hess 1986, Jansen and Hess 1989) being two particularly important transformations. The former transformation, truncated at order $1/c^2$, leads to the $H^{\text{SO}}$ operator used below. It is now possible to carry the Douglas–Kroll transformation to third or even higher orders (Nakajima and Hirao 2000a, b, Wolf *et al.* 2002). Kutzelnigg has explored the mathematical properties of the transformations in detail (Kutzelnigg 1989, 1990, 1997, Kutzelnigg and Liu 2000), and Dyall (2002) has recently given a summary of his papers on component elimination. A procedure known as relativistic elimination of small components (RESC) has also been considered recently (Nakajima and Hirao 1999, Nakajima *et al.* 1999). Nuclear gradient implementations exist for many of these elimination schemes, including the RESC scheme (Fedorov *et al.* 2001b) and Douglas–Kroll (de Jong *et al.* 2001). A number of workers stop after reducing the four-component equation to two by elimination of its small components, since this approach retains an explicit SOC during self-consistent field (SCF) orbital optimization. Often this is done for linear molecules, but a program has been developed recently for two-component calculations on polyatomic molecules (Fleig *et al.* 2001).

However, since most available programs for molecular quantum chemistry are single-component codes, solving the non-relativistic Schrödinger equation, it is reasonable to attempt to adapt these programs to include SO and other relativistic

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corrections. The Foldy–Wouthuysen transformation of the Dirac–Coulomb equations leads to the following operators, first the ordinary non-relativistic Schrödinger operator

$$H^{NR} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_i\sum_\alpha Z_\alpha e^2/r_{i\alpha} + \sum_i\sum_j e^2/r_{ij} + \sum_\alpha\sum_\beta Z_\alpha Z_\beta e^2/r_{\alpha\beta}, \quad (1)$$

and, at order $1/c^2$, the spin-independent mass–velocity and Darwin relativistic corrections (whose two-electron term is often neglected):

$$H^{MV} = -\frac{\hbar^4}{8c^2m^3}\sum_i \nabla_i^4\,, \quad (2)$$

$$H^D = -\frac{\pi\hbar^2}{2m^2c^2}\left[\sum_i\sum_\alpha Z_\alpha e^2\delta(r_{i\alpha}) + \sum_i\sum_j e^2\delta(r_{ij})\right]. \quad (3)$$

These are often termed 'scalar' relativistic effects and may be used to define a spin-free Hamiltonian, also known as the Cowan–Griffin (Cowan and Griffin1976) operator,

$$H^{\mathrm{SF}} = H^{\mathrm{NR}} + H^{\mathrm{MV}} + H^{\mathrm{D}}. \quad (4)$$

The final term at order $1/c^2$ is the SOC term, known as the Breit–Pauli SO operator,

$$H^{SO} = \frac{1}{2m^2c^2}\left[\sum_i\sum_\alpha \frac{Z_\alpha e^2}{r_{i\alpha}^3}\hat{\mathbf{l}}_{i\alpha}\cdot\hat{\mathbf{s}}_i - \sum_i\sum_j \frac{e^2}{r_{ij}^3}\hat{\mathbf{l}}_{ij}\cdot(\hat{\mathbf{s}}_i + 2\hat{\mathbf{s}}_j)\right], \quad (5)$$

which contains both one- and two-electron terms. In these formulae, $\hat{\mathbf{l}}$ and $\hat{\mathbf{s}}$ are space and spin angular momentum operators, $\hat{\mathbf{l}}_{i\alpha} \equiv (\mathbf{r}_i - \mathbf{R}_\alpha)\times\mathbf{p}_i, \hat{\mathbf{l}}_{ij} \equiv (\mathbf{r}_i - \mathbf{r}_j)\times\mathbf{p}_i$, Roman and Greek subscripts refer to electrons and nuclei respectively and the other symbols have their usual meanings. Schwarz *et al.* (1989) have considered the formal $Z$ dependence of these terms, and Tarczay *et al.* (2001) give very interesting and useful comparison of sizes of the spin-free and very small spin-dependent terms for close-shell, light molecules. Spin–spin coupling (see Langhoff and Kern 1977), which is also of order $1/c^2$ and is relevant to the zero field splitting observed in electron paramagnetic resonance (EPR) experiments, is not considered in this review.

Exclusion of electron–positron pair creations leads to the inclusion of kinematic multiplicative factors in each term of an operator that is otherwise identical to $H^{\mathrm{SO}}$ given above, which is termed the no-pair SO Hamiltonian (Samzow and Hess 1991). The latter may be used in a variational manner. However, the Breit–Pauli Hamiltonian is variationally unstable and thus must be used as a perturbation only (Hess *et al.* 1995).

In addition to two of the present authors (Fedorov and Gordon 2000), many have incorporated the Breit–Pauli $H^{\mathrm{SO}}$ into single-component programs. Among these are Klotz *et al.* (1984), Furlani and King (1985), Yarkony (1992), Havlas *et al.* (1998), Berning *et al.* (2000) and Malmqvist *et al.* (2002).

The two-electron term of the Breit–Pauli operator grows slowly as the nuclear charge $Z$ increases. In contrast, the one-electron term contains $Z$ both explicitly and implicitly through the $r_{i\alpha}^3$ reciprocal and thus grows rapidly with $Z$. This suggests an approximation in which the two-electron terms are omitted, and this is compensated for by treating $Z$ as an adjustable parameter $Z_{\mathrm{eff}}$. This approximation is considered

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in section 2.4. If the two-electron term is retained, it may be calculated completely. However, approximate treatments of the two-electron terms have been investigated, in order to improve computational time with as little sacrifice of accuracy as possible. Our approach (Fedorov and Gordon 2000) is to omit active–active two-electron contributions to the $H^{\mathrm{SO}}$ matrix elements, and this is compared with full computation of the two-electron term in section 2.5. Hess *et al.* (1996) approximate this term by defining a mean field operator by averaging the density of any unfilled valence orbitals and then neglecting all but the one-centre integrals in the two-electron term, only. Tatchen and Marian (1999) have evaluated the success of the last approach for light elements.

Finally, the entire Breit–Pauli operator may be approximated by an effective operator, inspired by core potential operators. The latter are typically extracted from relativistic wavefunctions for atoms by averaging the two potentials that generate the large component radial wavefunctions, labelled $j = l \pm 1/2$, to produce an averaged relativistic effective potential $U^{\mathrm{AREP}}$. These potentials permit even non-relativistic programs to include spin-free mass–velocity and Darwin effects. This use of the *average* of the potentials suggests that their *difference* preserves information about the SO effect. These SO operators are of the form

$$H^{\mathrm{SO}} = \sum_{l=1}^{L-1} \Delta U_l^{\mathrm{REP}} \left( \frac{l}{2l+1} \sum_{m=-l-1/2}^{l+1/2} |l, l+1/2, m\rangle\langle l, l+1/2, m| - \frac{l+1}{2l+1} \sum_{m=-l+1/2}^{l-1/2} |l, l-1/2, m\rangle\langle l, l-1/2, m| \right) \tag{6}$$

where the differences in the radial potentials

$$\Delta U_l^{\mathrm{REP}} = U_{l,l+1/2}^{\mathrm{REP}}(r) - U_{l,l-1/2}^{\mathrm{REP}}(r) \tag{7}$$

are typically expanded in Gaussians and require a modified version of the core potential integrals (Pitzer and Winter 1991). Several different families of effective SO potentials have been generated in this way such as ECPs based on the Cowan–Griffin equation, which have been reviewed by Ermler *et al.* (1988), and *ab initio* model potentials (AIMPs) representing the Wood–Boring operator (Seijo 1995, Seijo *et al.* 2001). Alternatively, the SOC contribution from the core electrons removed by a potential can be computed on the fly, using atomic core and molecular valence orbitals, without any need for fitting a potential to purely atomic data, as was developed for model core potentials (Krause and Klobukowski 1996, Fedorov and Klobukowski 2002). The latter are considered in section 2.6.

Obviously, an important question about SOC is what its effect is on molecular structures. Because of concern about the variational stability of the Breit–Pauli operator (Hess *et al.* 1995), it is normally used as a perturbative term following a non-relativistic or spin-free relativistic wavefunction determination. This *a posteriori* approach means that little work has been done on nuclear gradients including SO effects. We are aware of only two recent attempts to program nuclear gradients including SOC. Han *et al.* (1998) include an ECP operator of the form of equation (6) variationally in a two-component RHF wavefunction and develop an analytic gradient for it, except that the integral derivatives of the SO operator are obtained by a numerical differentiation. Matsika and Yarkony (2001, 2002) have included the

Breit–Pauli operator via quasi-degenerate perturbation theory in their formalism for locating conical intersections and other interesting features along seam crossings.

Of course, one may also investigate the effect of SOC on structures by purely numerical means, from the energies only, so a few examples may be given. Han *et al.* (1998) found that the inclusion of SOC shortens the bond distance of $PbH^+$ from 1.813 to 1.793 Å, whereas in the closed-shell system $PbH_4$ there is almost no effect: from 1.740 to 1.737 Å. High level calculations (Flores and Gomez 2002) predict a very small energy preference for a bent HCCCS radical over linear, but an SOC stabilization of $300 \times 10^{-6} E_h$ at linear geometries versus $10 \times 10^{-6} E_h$ at bent geometries reverses the energy order from a prediction for a linear molecule, in agreement with experiment. Two-component zeroth order regular approximation (ZORA) computations (Liu *et al.* 2001) for a number of lead compounds show that SOC has effects similar to their results for $Pb_2$, for which $r_e$ increases by 0.048 Å, $D_e$ decreases by 1.22 eV, and $\omega_e$ decreases by $21\,\mathrm{cm}^{-1}$. It is safe to say that SOC effects on molecular geometries and other potential surface parameters will be larger for open-shell systems and/or those containing heavy atoms. Additional work on the inclusion of SOC in the variational wavefunction optimization and implementation of nuclear gradient codes including this term is clearly desirable.

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No matter what form of SO operator is chosen, one must evaluate the coupling of states that are usually but not always of different multiplicity. This may be done by perturbation theory (Havriliak and Yarkony 1985, Yarkony 1986) but is most often done by configuration interaction (CI) calculations (Battle and Gould 1993, Sjøvoll *et al.* 1997, Mitrushenkov and Palmieri 1997, Yabushita *et al.* 1999, Jansen *et al.* 1999, Berning *et al.* 2000, Tilson *et al.* 2000), evaluating $H^{NR} + H^{SO}$ or $H^{SF} + H^{SO}$ matrix elements between the states. Matrix elements over the Breit–Pauli $H^{SO}$ operator introduce new integrals to be evaluated, related to derivatives of ordinary integrals (e.g. King and Furlani 1988, Bearpark *et al.* 1992). The orbitals for all of these methods are usually optimized with an appropriate multiconfigurational SCF (MCSCF) wavefunction, typically of the complete active space (CAS) SCF (CASSCF) type (Schmidt and Gordon 1998).

If only one singlet and one triplet configuration are included, one must evaluate $H^{SO}$ elements between the singlet and all three spin functions of the triplet state, $\alpha\alpha$, $\alpha\beta + \beta\alpha$ and $\beta\beta$. As the number of these matrix elements gets large quickly with increased CI spaces, it is useful to exploit symmetry to minimize the computational effort, and this is discussed in section 2.3. The SO CI (SOCI) calculation may be done in a basis of determinants or configurations, or in a state basis (Hay 1982) where only a few of the low lying states (expanded in a larger determinant or configuration space) are kept. Working in the state basis reduces the amount of time required for $H^{SO}$ matrix evaluation by knowing which configurations have small CI coefficients, and of course it leads to a much smaller diagonalization, in the spirit of 'internally contracted' CI. Of course, increasing the number of states included in the model space leads eventually to the same result as working in the full CI space, but the use of small model spaces greatly reduces the effort. Many calculations cited in this work are based on that latter approach. These are denoted by SO-CASCI (or SO-MRCIS or SO-MRCISD) for the Hamiltonian matrix constructed in the basis of a few selected CASCI (or multireference CI with single (MRCIS) or with single and double (MRCISD) excitations) states.

The idea of working in the state basis suggests an alternative to the use of SOCI, namely inclusion of SO into multireference perturbation theory, with the SOC perturbations now included into the effective Hamiltonian. This is considered in detail in section 2.7. SO multiconfigurational quasi-degenerate perturbation theory (SO-MCQDPT) is based on single and double excitations from the CAS and the SOC Hamiltonian is constructed in the basis of a few CASCI states, with the perturbations now built into the effective SOC Hamiltonian.

The result of an SOCI of any type is a spin-mixed wavefunction, in which the degree of mixing of different spin states depends on the size of the $H^{SO}$ interaction and the energy difference between the original Russell–Saunders states. The degree of mixing governs the extent to which ISCs may occur. Transition moments between spin-mixed states may be computed, as illustrated in section 3.3, yielding phosphorescence rates.

### 2.2. *Phenomenological spin–orbit coupling and chemical reactions*

In order to examine the effect of SOC on energies of chemical reactions it is useful to consider the phenomenological operator that is given by $\hat{H}^{SO} = A(r)(LS)$ where $L$ and $S$ are the total angular and spin momenta and $A(r)$ is some radial dependence operator. While this operator is known to possess somewhat different symmetry properties and it should not be used for *ab initio* calculations of general molecules it is of use in understanding qualitative SO splitting in atoms or even diatomic molecules.

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Suppose one has a chemical reaction $A + B \rightarrow C + D$ and one wants to know how large the SOC effect is on the reaction enthalpy, relative to doing a quantum chemical calculation without SOC. In general, the SOC effects may be manifold:

(1) The total ground state energy of each species can be directly affected.
(2) The minimum geometry is affected by the change in the energy.
(3) Excited states can interact with the ground state, shifting its energy.
(4) Excited states may also be split by SOC. Excited state energies directly affect the heat of chemical reactions through electronic partition functions (see below).

Let us focus on the case without very heavy atoms; H–Xe may fall into this category. In this case (b) can usually be neglected. Consider the other three issues listed above in some detail.

(a) Naturally, only states with some degeneracy can be split. The vast majority of stable compounds have singlet ground states and belong to the totally symmetric irreducible representation, and hence the SOC effect can be confidently expected to be small. Diatomic molecules are probably the most common exception, since for such species degenerate states are not unusual. Atoms, on the other hand, typically have degenerate ground states. In this case the phenomenological operator $\hat{H}^{SO} = A(r)(LS) = \frac{1}{2}A(r)(J^2 - L^2 - S^2)$ is useful, where $J$ is the total angular momentum $J = L + S$. By computing eigenvalues of this operator in the $LS$ coupling scheme, one obtains the SOC shifts to first order, i.e.

$$\begin{aligned} E(JLS) &= E(LS) + \left\langle JLS \middle| \hat{H}^{SO} \middle| JLS \right\rangle \\ &= E(LS) + \tfrac{1}{2}A[J(J+1) - L(L+1) - S(S+1)], \end{aligned} \tag{8}$$

where $A$ is a constant and we use atomic units. Suppose that a chemical reaction involves formation of a fluorine atom. By looking up experimental energy levels

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(e.g. Moore 1949, 1952, 1958), one finds that the *LS* state $^2$P is split into $^2$P$_{3/2}$ and $^2$P$_{1/2}$. The ground state is then $^2$P$_{3/2}$ and its energy is shifted by 134.7 cm$^{-1}$ or 0.38 kcal mol$^{-1}$ relative to (lower than) the $^2$P state. Chemical accuracy is often considered to be 1 kcal mol$^{-1}$ (e.g. Curtiss *et al.* 1998) so even for this very light atom SOC makes a non-negligible contribution to reaction enthalpies. To obtain this value for F, one first calculates $A$: $E(J, L, S) - E(J-1, L, S) = AJ$ (this relation is known as the Landé interval rule), and thus $E(J = 3/2, L = 1, S = 1/2) - E(J = 1/2, L = 1, S = 1/2) = 3A/2 = -404.10\,(\text{cm}^{-1})$ and hence $A = -2/3 \times 404.10\,(\text{cm}^{-1})$. As given by equation (8), $E(^2\text{P}_{3/2}) = A/2$ relative to $E(^2\text{P})$, and thus one obtains the value of $-134.7$ cm$^{-1}$. This number can be easily computed theoretically as well. Incidentally, halogen atoms appear to have the largest SOC splitting among the main group elements within each row. In the case of molecules, however, the effect can vary greatly depending on the details of the electronic structure. For example, as found by Fedorov *et al.* (1999, 2001a), in $\text{O}_2^+$ the ground and excited $^2\Pi$ states have very different splittings of 200. (X $^2\Pi_g$) and 3.5 cm$^{-1}$ (A $^2\Pi_u$).

(c) For main group elements the effects of such off-diagonal coupling are usually fairly small. The situation is quite different for transition metals with many tightly packed electronic states arising from open d and f shells. As an example, consider the group 14 main group elements C–Pb. According to calculations described below, the coupling of excited states to the ground state increases the splitting $^3$P$_0$–$^3$P$_2$ by 0.1 (C), 2.5 (Si), 84.9 (Ge), 507.8 (Sn) and 4101. (Pb) cm$^{-1}$ or relative to the experimental splitting 0.6% (C), 3.2% (Si), 15.2% (Ge), 30.0% (Sn) and 52.4% (Pb). As expected the effect grows quickly with atomic charge.

(d) In order to estimate electronic partition functions some simple *ab initio* atomic calculations were performed. The all-electron basis sets were taken from an unrelated study (Lie *et al.* 2002) and all states coming from the s$^2$p$^2$ configuration of C–Pb, namely $^3$P, $^1$S and $^1$D, were coupled using SO-MCQDPT, based on the double valence active space of 4 electrons in 8 orbitals, chosen to include 4 valence *n*s*n*p and 4 virtual $(n+1)$s$(n+1)$p orbitals in order to treat electron correlation properly.

The electronic partition function is given by

$$Z_{\text{el}} = \sum_{i=0}^{\infty} g_i \exp\left(-\frac{E_i}{RT}\right), \tag{9}$$

where $g_i$ is the degeneracy of an electronic level having energy $E_i$ (relative to $E_0 = 0$). From $Z_{\text{el}}$ one can easily compute free energies, for example, the electronic contribution to the Gibbs free energy:

$$G_{\text{el}} = -RT \ln Z_{\text{el}}. \tag{10}$$

If the ground state is well separated from the excited states (meaning that the exponent prefactor for all excited states is close to 0), then $G_{\text{el}}$ is simply given by $-RT \ln g_0$. Adding excited states in general makes $G_{\text{el}}$ more negative, because of the larger $Z_{\text{el}}$ that is always positive. Enthalpy (or internal energy) behaves differently; it is given by

$$H_{\text{el}} = E_{\text{el}} = \frac{1}{Z_{\text{el}}} \sum_{i=0}^{\infty} g_i E_i \exp\left(-\frac{E_i}{RT}\right). \tag{11}$$

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In particular, if excited states are neglected, then $E_0$ and thus $H_{\rm el}$ are zero. This means that the electronic partition function effects at low temperature enter thermochemistry primarily through the entropy.

If SOC effects are neglected, the excited states are high in energy, and the ground state degeneracy does not change for all reactants and products (a fairly common occurrence for closed-shell molecules composed of light atoms), then the contribution of the electronic partition function to the reaction energies is close to zero.

Next, consider the effect of SOC on electronic partition functions, using the main group 14 elements as examples. *Ab initio* calculations or experimental data reveal that for all of these atoms the lowest *LS* states are well separated. In fact, the separation changes little with atomic number for Si–Pb: in each case, the $^3$P state is the ground state, and the first excited state, $^1$D, is 30.2 (C), 18.4 (Si), 18.0 (Ge), 16.2 (Sn) and 19.1 (Pb) kcal mol$^{-1}$ higher. The second excited $^1$S state is 30.7 (C), 23.9 (Si), 25.3 (Ge), 24.2 (Sn), 26.7 (Pb) kcal mol$^{-1}$ higher relative to $^1$D. Thus a very good estimate of the spin-free electronic sum would be $-RT\ln 9$, growing linearly with temperature (9 is the product of the space and spin degeneracy of $^3$P).

When SOC is included in the calculations, the *LS* levels are split and coupled. As expected, the SOC is small for C and large for Pb. In the case of C, although the formerly degenerate nine substates of $^3$P state are split into $5+3+1$-fold degenerate levels $^3\mathrm{P}_2$, $^3\mathrm{P}_1$ and $^3\mathrm{P}_0$, the splitting is small and so the exponent factors are close to 1; thus, one recovers approximately $Z_{\rm el}=\ln 9$. As the atomic charge increases, the exponential factors appreciably decrease $Z_{\rm el}$. The values of $G_{\rm el}$ are plotted in figures 1(*a*)–1(*c*). It is clear that the spin-free values are nearly a straight line and SOC effects make $G_{\rm el}$ less negative at room temperature by 1–2 kcal mol$^{-1}$. This difference directly adds to the Gibbs' reaction energy.

Similar calculations can be performed for molecules. Consider XH, where X = Ti, Zr and Hf. We couple the same states and use the same basis set as in a previous study by Koseki *et al.* (2001b). The ground states are a quartet for Ti and a doublet for Zr and Hf; thus one can see that the slope at low temperature for spin-free values is different (figures 1(*d*)–1(*f*)). Secondly, a large number of low lying excited states cause the $G_{\rm el}$ dependence on $T$ to depart from linearity.

As expected, the effect of excited states and thus SOC effects grow rapidly with temperature. As a word of caution, one should remember that at high temperature commonly used approximations (e.g. harmonic oscillator, rigid rotor, ideal gas model) for computing partition functions start to become less applicable. Possibly the most important among these is anharmonicity. Especially for small molecules or for isolated modes, anharmonicity can be accounted for with additional effort (e.g. Chaban *et al.* 1999).

In conclusion, we suggest the reader consider the above factors and decide whether the sought-after accuracy permits the neglect of SOC effects for a given reaction.

### 2.3. *Symmetry in spin–orbit coupling*

Computation of SOC requires evaluation of matrix elements of the operator $H^{\rm SO}$ between configurations or states, in order to perform the SOCI. No matter what form of the $H^{\rm SO}$ operator as described in section 2.1 is chosen, adding this SOC term changes the symmetry properties of the Hamiltonian $H^{\rm NR}+H^{\rm SO}$ or $H^{\rm SF}+H^{\rm SO}$. Since the number of such matrix elements of $H^{\rm SO}$ can be very large, it is useful to

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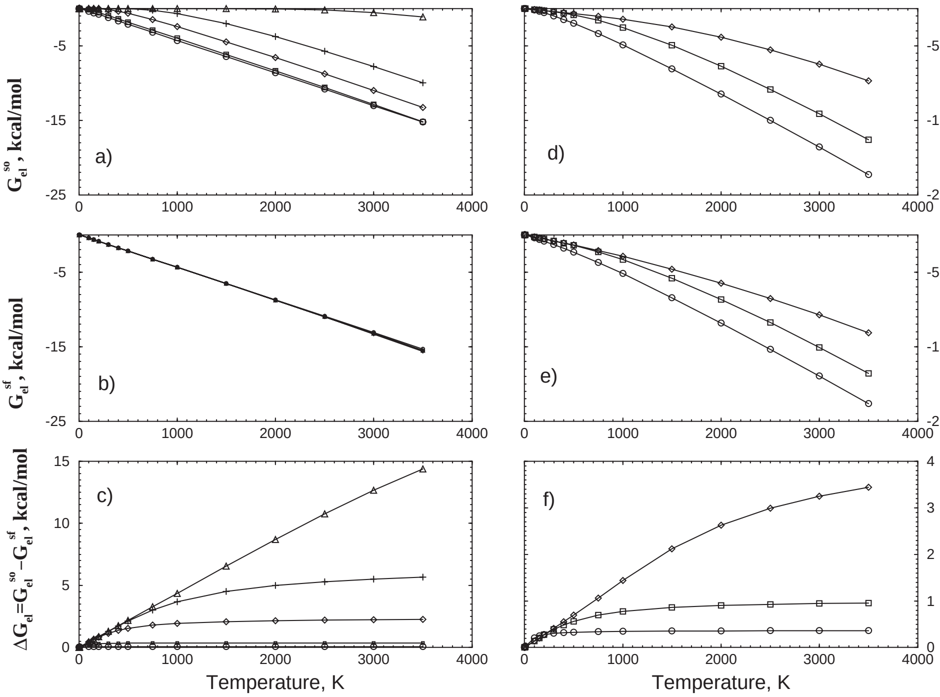

Figure 1. Temperature dependence of electronic Gibbs' energies for (*a*) C–Pb with SOC, (*b*) C–Pb without SOC, (*c*) difference (SOC effect) for C–Pb, where atoms are marked as C (circles), Si (squares), Ge (diamonds), Sn (pluses), Pb (triangles), (*d*) TiH, ZrH, HfH with SOC, (*e*) TiH, ZrH, HfH without SOC, (*f*) difference (SOC effect) for TiH, ZrH, HfH, where molecules are marked as TiH (circles), ZrH (squares) and HfH (diamonds).

exploit symmetry in order to avoid computing the numerous zero elements and, wherever possible, to generate elements related to other elements by simple formulae.

A thorough review of the symmetry properties of $H^{\mathrm{SO}}$ was given by Fedorov and Gordon (2002). In atoms, instead of orbital ($L$) and spin ($S$) angular momenta, the total momentum $J = L + S$ is conserved. The symmetry group of atoms is $\mathrm{K_h}$ with or without SOC. In the case of molecules, however, the symmetry with SOC is described by either point groups (integer spin) or double groups (half-integer spin). Rotation by an angle $\alpha$ around an axis given by a normalized vector $\mathbf{n}$ can be written as $\exp[-i\alpha(\hat{\mathbf{J}} \cdot \mathbf{n})]$, where $\mathbf{J}$ is the angular momentum operator, and it is obvious that, for half-integer momentum $J$, rotations by $\alpha$ and $\alpha + 2\pi$ differ by sign. The double groups thus have twice as many elements as the point groups, corresponding to having elements $\alpha + \gamma$ (in the Euler angle ($\alpha$, $\beta$, $\gamma$) representation) and $\alpha + \gamma + 2\pi$. Double groups, however, are not direct products of the point groups times a group containing two elements. Rather, the multiplication algebra of the double groups follows the angular momentum properties. The irreducible representations of the double groups contain all those irreducible representations for the corresponding point group (called single valued) and some additional (double-valued) representations that are very often degenerate. The double-valued representations can easily be obtained by reduction of the irreducible representations of $\mathrm{K_h}$ with half-integer spin onto the given molecular group. For example, the $C_{2v}$ double group is not Abelian and contains four non-degenerate single-valued and one two-fold degenerate double-valued irreducible representations. The double groups that arise when SOC is considered are exactly the same as the factor groups of the space groups in crystals. In the latter case translation by a fraction of the period gives rise to doubling of the group elements for non-symmorphic groups. More details on the use of double groups in SOC calculations can be found in Marian (2001).

For practical purposes it is convenient to formulate selection rules for the SOC matrix elements. The rules differ somewhat, depending on how one constructs the bra and ket states. The most convenient approach is to take the '*LS*' states (that is, states coming from computations with the spin-free Hamiltonian, not necessarily atomic) as the basis states. Then one can easily add code for computing their SOC matrix elements to a conventional quantum chemistry program. There is some advantage in the alternative of taking linear combinations of the '*LS*' terms, for example, by constructing such combinations that transform as the irreducible representations of the double groups. This allows block diagonalization of the SOC Hamiltonian matrix that can be useful for large SOCI. Another choice is to make the Hamiltonian matrix real by taking linear combinations that have definite time reversal symmetry (not possible for some point groups). In any case, such linear combinations reduce the diagonalization cost but ultimately one still has to compute matrix elements for the '*LS*' terms.

The general SOC matrix element can be written as

$$\langle \alpha \Gamma i S M_S \, | H^{\mathrm{SO}} | \, \alpha' \Gamma i' S' M_S' \rangle, \tag{12}$$

where the SOC Hamiltonian $H^{\mathrm{SO}}$ might be the full Breit–Pauli operator given by equation (5), containing both one- and two-electron operators, or the semi-empirical $Z_{\mathrm{eff}}$ form containing only the one-electron term discussed below. The state $|\alpha \Gamma i S M_S\rangle$ contains the symmetry labels of the wavefunction obtained from a conventional spin-independent calculation: $\Gamma$ denotes the irreducible representation of the point group $G$ of the molecule, $i$ distinguishes degenerate components of $\Gamma$, $\alpha$ distinguishes equivalent irreducible representation and $S(S+1)$ and $M_S$ are the eigenvalues (in atomic units) of the spin operators $\hat{S}^2$ and $\hat{S}_z$ respectively.

Now we summarize the selection rules for the SOC matrix elements, which can be derived from the Wigner–Eckart theorem and the Hermitian properties of the SOC Hamiltonian.

The SOC matrix element is zero if any of the following is satisfied:

(1) *Rules due to spin momentum*

- (a) both bra and ket are singlets ($S=0$ and $S'=0$);
- (b) spins for bra and ket differ by more than unity ($|S-S'|>1$);
- (c) spin projection on the $z$-axis of bra and ket differ by more than unity ($|M_S-M_S'|>1$);
- (d) bra is equal to ket and both states are represented by a real-valued (or purely imaginary) wavefunction;
- (e) either only bra or only ket has half-integer $S$ ($S+S'$ is half integer).

(2) *Rule due to spatial part (angular momentum for atoms)*

- (a) the product $\Gamma \times \Gamma^L \times \Gamma'$ does not contain the totally symmetric representation.

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$\Gamma^L$ are the irreducible representations to which the three components $x$, $y$ and $z$ of the angular momentum $L$ belong. (For atoms this rule duplicates rules 1(*a*)–1(*c*), with the replacement of spin by angular momentum; for linear molecules the matrix element is zero if $|L_z - L_z'| > 1$. In addition, for both atoms and molecules with an inversion centre, parity is conserved, that is terms of different parity do not mix.)

Instead of separating spin and orbital symmetries as above, one can determine whether a SOC matrix element is zero using the double group symmetry. In this case, since $H^{\mathrm{SO}}$ belongs to the totally symmetric representation, the product $\Gamma \times \Gamma^L \times \Gamma'$ is reduced to $\Gamma \times \Gamma'$. The rules due to spin momentum are in general lost if the bra and ket represent spin-mixed states. It was found (Fedorov and Gordon 2002) that, if the bra and ket are states coming directly from a calculation using the spin-free Hamiltonian, then using such double-group rules is disadvantageous compared with the rules given above.

Using symmetry properties related to spin rotations, at most three elements need to be explicitly calculated, given $S$ and $S'$:

$$\langle \alpha \Gamma i S M'_S - 1 \,|\, H^{\mathrm{SO}} | \alpha' \Gamma' i' S' M'_S \rangle = -(S', 1, M'_S, -1 | S, M'_S - 1) \langle \alpha \Gamma i S | \hat{L}_+ \hat{S} | \alpha' \Gamma' i' S' \rangle, \quad (13)$$

$$\langle \alpha \Gamma i S M'_S | H^{\mathrm{SO}} | \alpha' \Gamma' i' S' M'_S \rangle = (S', 1, M'_S, 0 | S, M'_S) \langle \alpha \Gamma i S | \hat{L}_0 \hat{S} | \alpha' \Gamma' i' S' \rangle, \quad (14)$$

$$\langle \alpha \Gamma i S M'_S + 1 | H^{\mathrm{SO}} | \alpha' \Gamma' i' S' M'_S \rangle = -(S', 1, M'_S, +1 | S, M'_S + 1) \langle \alpha \Gamma i S | \hat{L}_- \hat{S} | \alpha' \Gamma' i' S' \rangle. \quad (15)$$

In equations (13)–(15), the quantities in parentheses are the Clebsch–Gordan coefficients. The remaining elements are zero if $|M_S - M_S'| > 1$, or they can be computed from the above three generators by simple scaling with ratios of the Clebsch–Gordan coefficients, e.g.

$$\left\langle \alpha\, \Gamma i S M_S - 1 | H^{\mathrm{SO}} | \alpha' \Gamma' i S' M_S \right\rangle = -(S', 1, M_S, -1 | S, M_S - 1) \left\langle \alpha\, \Gamma i S | \hat{L}_+ S | \alpha' \Gamma' i S' \right\rangle \Big/ (S', 1, M'_S, -1 | S, M'_S - 1), \quad (16)$$

where the reduced matrix element is calculated from the above defining relation (for $M'_S$). Some Clebsch–Gordan coefficients are equal to zero; however, using the largest possible $M_S$, that is $M_S = S$, $M'_S = S'$, always leads to non-zero Clebsch–Gordan coefficients, thus avoiding division by zero.

If the wavefunction is real valued (or purely imaginary valued), then only two rather than three elements have to be computed, as there is a simple relation as follows (given separately for $S' = S$ and $S' = S+1$):

$$\left\langle \alpha \Gamma i S M_S | H^{\mathrm{SO}} | \alpha' \Gamma' i' S + 1, M_S + 1 \right\rangle = \left\langle \alpha \Gamma i S, -M_S | H^{\mathrm{SO}} | a' \Gamma' i' S + 1, -M_S - 1 \right\rangle^* \quad (17)$$

$$\left\langle \alpha \Gamma i S M_S - 1 | H^{\mathrm{SO}} | \alpha' \Gamma' i' S M_S \right\rangle = -\left\langle \alpha \Gamma i S M_S | H^{\mathrm{SO}} | \alpha' \Gamma' i' S M_S - 1 \right\rangle^* \quad (18)$$

The detailed structure of the SOC Hamiltonian is provided below. The cases of equal and different multiplicities are given separately in tables 1 and 2. The orbital part is assumed to be different for the two states. The only two matrix elements which need to be explicitly calculated are $A$ and $B$, as the rest can be obtained from these two.

The eigenstates of the SOC Hamiltonian are classified according to the double point group symmetry, for example in atoms by the labels $J^2$ and $J_z$.

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Table 1. $H^{\mathrm{SO}}$ matrix for equal multiplicities.

| | $S$ | $S-1$ | $S-2$ | ... | $\leftarrow M'_S$ |
|---|---|---|---|---|---|
| $S$ | $A$ | $-B^*$ | 0 | 0 | 0 |
| $S-1$ | $B$ | $aA$ | $-bB^*$ | 0 | 0 |
| $S-2$ | 0 | $bB^*$ | ... | ... | 0 |
| ... | 0 | 0 | ... | ... | ... |
| $M_S \uparrow$ | 0 | 0 | 0 | ... | ... |

$A$,$B$—calculated matrix elements, while $a$ and $b$ are ratios of the Clebsch–Gordan coefficients: $a = (S, 1, S-1, 0|S, S-1)/(S, 1, S, 0|S, S)$ and $b = (S, 1, S-1, -1|S, S-2)/(S, 1, S, -1|S, S-1)$. "..." denotes further propagation of $A$ and $B$ by means of equation (16).

Table 2. $H^{\mathrm{SO}}$ matrix for different multiplicities.

| | $S+1$ | $S$ | $S-1$ | ... | $\leftarrow M'_S \rightarrow$ | $-S$ | $-S-1$ |
|---|---|---|---|---|---|---|---|
| $S$ | $B$ | $A$ | $bB^*$ | 0 | 0 | 0 | 0 |
| $S-1$ | 0 | $aB$ | $cA$ | ... | 0 | 0 | 0 |
| $S-2$ | 0 | 0 | ... | ... | ... | 0 | 0 |
| $M_S\uparrow$ | 0 | 0 | 0 | ... | ... | ... | 0 |
| $-S$ | 0 | 0 | 0 | 0 | ... | ... | $B^*$ |

$A$,$B$—calculated matrix elements and $a$, $b$, $c$ are ratios of the Clebsch–Gordon coefficients: $a = (S+1, 1, S, -1|S, S-1)/(S+1, 1, S+1, -1|S, S)$, $b = (S+1, 1, S-1, 1|S, S)/(S+1, 1, -S-1, 1|S, -S)$, $c = (S+1, 1, S-1, 0|S, S-1)/(S+1, 1, S, 0|S, S)$.

### 2.4. *Effective charge approach*

The effective nuclear charge ($Z_{\mathrm{eff}}$) approximation is the simplest method available for the qualitative computation of SOC effects in molecules. The $Z_{\mathrm{eff}}$ approximation consists of using only the one-electron term from the Breit–Pauli Hamiltonian given in equation (5):

$$H^{\mathrm{SO}} = \frac{e^2}{2m^2c^2} \sum_{i=1}^{N_{\mathrm{el}}} \sum_{\alpha=1}^{N_{\mathrm{atom}}} \frac{Z_{\mathrm{eff}}(\alpha)}{r_{i\alpha}^3} \mathbf{l}_{i\alpha} \cdot \mathbf{s}_i, \tag{19}$$

in which the nuclear charges $Z_\alpha$ have been replaced by empirical parameters $Z_{\mathrm{eff}}(\alpha)$. The motivation for this is two-fold: (a) the success of the Landé interval rule $A\mathbf{L} \cdot \mathbf{S}$ in fitting observed atomic spectra (as discussed in section 2.2; see also Condon and Shortley (1935) regarding atomic SOC) and (b) the understanding that the two-electron term grows more slowly than the one-electron term of $H^{\mathrm{SO}}$, as discussed in section 2.5. The parameters $Z_{\mathrm{eff}}(\alpha)$ are determined by fitting this operator to some experimental SO splitting, most often some atomic state. One relies on the hope that deviations from the true nuclear charges $Z_\alpha$ will compensate for the error of neglecting the two-electron terms.

This approximation has its roots in the transferability of atomic SOCs into molecules, as suggested by McClure (1949). The $r^{-3}$ dependence of the operator means that the coupling is dominated by the interior shape of valence orbitals, which are not greatly modified by bonding. The $Z_{\mathrm{eff}}$ approximation has been employed by many workers including Stone (1963), Ishiguro and Kobori (1967), Hay *et al.* (1979), Cohen *et al.* (1979), Wadt (1981, 1982), Yabushita and Morokuma (1988) and Heinemann *et al.* (1995a, b). The idea has received theoretical justification from Moores and McWeeny (1973) who pointed out that for spherically symmetric atoms a $\zeta(r)\,\mathbf{L}\cdot\mathbf{S}$ form is equivalent to the entire operator, and who therefore concluded that the use of good wavefunctions is more important than the exact evaluation of all terms in the SO operator. Hinkley *et al.* (1972) also noted that two-centre contributions are small because of cancellation between the two-center one- and two-electron terms. Therefore, the $Z_{\mathrm{eff}}$ approximation is considered to be an effective means to estimate SOC effects in molecules.

A complication arises when ECP calculations are employed, as is frequently the case for heavy elements, since the use of averaged relativistic potentials readily incorporates spin-free relativistic effects. However, ECP orbitals go to zero at the nuclei and lack the correct radial nodal structure (although one such node may be present when semi-core potentials are used) and, therefore, are very different in shape from all-electron orbitals in the small $r$ region. This is crucial for the expectation value of the one-electron term of $H^{\mathrm{SO}}$ because of its $r^{-3}$ dependence, and results in very small splittings unless rather large $Z_{\mathrm{eff}}$ parameters are used (Wadt 1982, Klobukowski 1991). A convincing demonstration of this can be found in figures 3 and 4 of Stevens and Krauss (1982). The use of large $Z_{\mathrm{eff}}$ values reduces their physical interpretation from being a small adjustment to the true nuclear charge that compensates roughly for the neglect of the two-electron term to simply being recognized as empirical parameters. Consequently, the reliability and justification of the $Z_{\mathrm{eff}}$ approximation can be questioned. However, as described in this section, this approximation is a viable approach for introducing SOC effects in molecules in a semiquantitative fashion, as concluded by Wadt (1982).

Systematic studies of the $Z_{\mathrm{eff}}$ approach for the majority of the periodic table began with Koseki *et al.* (1992), who determined the $Z_{\mathrm{eff}}$ values for the second- and third-row main group elements using the all-electron basis sets 6-31G(d). Because of the absence of basis sets of similar quality for heavier elements, and a desire to use relativistic core potentials so that spin-free relativistic effects are also included, Koseki *et al.* (1995) determined $Z_{\mathrm{eff}}$ values for the main group elements using the SBKJC family of core potentials and basis sets (Stevens *et al.* 1984, 1992). The $Z_{\mathrm{eff}}$ parameters for the transition metals and sixth-row main group elements were given by Koseki *et al.* (1998), using the same SBKJC ECP family. A comparison of using the $\mathrm{Z}_{\mathrm{eff}}$ operator *versus* using the full Breit–Pauli $H^{\mathrm{SO}}$ for transition metals was given by Koseki *et al.* (2001a). For the main group elements, in contrast to most previous workers, these $Z_{\mathrm{eff}}$ values were obtained by reproducing the observed splittings in some low lying state of the monohydrides rather than an atom state, as the intended use of these parameters is in molecules. For transition metals, there are insufficient experimental data to obtain $Z_{\mathrm{eff}}$ from molecular data, and therefore the parameters were obtained by fitting appropriate atomic states. Tables 3 and 4 contain the $Z_{\mathrm{eff}}$ parameters for main group and transition metal elements respectively.

As expected, the few $Z_{\mathrm{eff}}$ parameters given for all electron (AE) basis sets in these tables are similar to the true nuclear charges but are slightly smaller. For carbon, the one-electron term is typically about twice as large as the two-electron term and is of opposite sign. Thus a value of $Z_{\mathrm{eff}} = 3.6$ replacing $Z = 6$ makes physical sense. While these data were obtained with the 6-31G basis set, these values should be transferable to any other all electron basis.

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Table 3. Effective nuclear charges for main group elements[a].

| Row | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18[b] |
|---|---|---|---|---|---|---|---|---|
| 2 | Li<br>(1.35)<br>1.5 | Be<br>(2.00)<br>2.2 | B<br>(2.75)<br>3.0 | C<br>(3.60)<br>3.9 | N<br>(4.55)<br>4.9 | O<br>(5.60)<br>6.0 | F<br>(6.75)<br>7.2 | Ne<br>(8.00)<br>8.5 |
| 3 | Na<br>(10.04)<br>132 | Mg<br>(10.80)<br>144 | Al<br>(11.53)<br>156 | Si<br>(12.25)<br>168 | P<br>(12.94)<br>180 | S<br>(13.60)<br>192 | Cl<br>(14.24)<br>204 | Ar<br>(14.85)<br>216 |
| 4 | K<br>779 | Ca<br>820 | Ga<br>341 | Ge<br>1312 | As<br>1353 | Se<br>1394 | Br<br>1435 | Kr<br>1476 |
| 5 | Rb<br>4070 | Sr<br>4180 | In<br>1617 | Sn<br>5500 | Sb<br>5610 | Te<br>5720 | I<br>5830 | Xe<br>5940 |
| 6 | Cs<br>12 210 | Ba<br>12 432 | Tl<br>9153 | Pb<br>18 204 | Bi<br>18 426 | Po<br>18 648 | At<br>18 870 | Rn |

[a] Values in parentheses are for use with all electron basis sets, while other values are meant for use with the SBKJC effective core potential family.

[b] Values given for the rare gases are obtained by extrapolation of linear relationships found for the other main group elements. Cohen *et al.* (1979) give alternative values for a few rare gases, obtained in their cations.

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Table 4. Effective nuclear charges for transition elements[a].

| | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Sc<br>8.6 | Ti<br>9.6 | V<br>10.6 | Cr<br>11.6 | Mn<br>12.8 | Fe<br>13.9 | Co<br>15.1 | Ni<br>16.4 | Cu<br>17.7 | Zn<br>(19.0)<br>330 |
| 2 | Y<br>185 | Zr<br>192 | Nb<br>199 | Mo<br>207 | Tc<br>214 | Ru<br>222 | Rh<br>230 | Pd<br>237 | Ag<br>245 | Cd<br>(253)<br>1584 |
| 3 | La<br>804 | Hf<br>1025 | Ta<br>1050 | W<br>1074 | Re<br>1100 | Os<br>1125 | Ir<br>1150 | Pt<br>1176 | Au<br>1202 | Hg<br>(1229)<br>9040 |

[a] Values are meant for use with the SBKJC effective core potential family.

[b] Values in parentheses are obtained by linear relationships with other transition metals and may be useful if excited states of these involve d electrons. In most cases the other value, obtained from extension of the main group elements, is more appropriate. See text.

In contrast, the parameters for use with the SBKJC ECPs are much larger than the true nuclear charges, with some exceptions. As already mentioned, the parameter is now also correcting for the poor representation of the inner portion of the valence orbitals, containing the unpaired electrons being coupled by the SO effect. These orbitals are now nodeless, with even the s orbitals going to zero at small $r$, so a larger $Z_{\text{eff}}$ is needed to compensate for the low electron density at small $r$. Those elements in which there is no core orbital lying below the unfilled valence orbital, namely the 2p and 3d elements, do not show such pronounced increases in their parameters, because their valence orbitals are more or less the correct shape at small $r$. The use of

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the semi-core potentials for Ga, In and Tl, which retain one extra core orbital, is responsible for their values differing from those of the adjacent full-core main group element. The SBKJC effective charges presented in these tables should not be transferred to other ECP basis sets sets, unless the same choice of how many core orbitals are removed by the potential has been made.

The effective nuclear charges were determined by fitting experimental data for monohydrides or, for the case of the transition metals, a few atomic states. Therefore, a simple test of these values is how well they reproduce the large number of atomic spectral terms that are available. Figure 2 plots the percentage difference between calculated and experimental energy splittings of as many atomic states as possible. Positive or negative values indicate whether the $Z_{\mathrm{eff}}$ approximation over- or underestimates the splittings. Most of the errors fall in the range of 30%, with transition metals, excited states and the heavier elements being more likely to fall outside this range. Koseki *et al.* (1992, 1995, 1998, 2001a) discuss the larger errors in some detail, so only a broad summary is presented here.

Errors of more than 100% are observed for Li, Be, N and Te. In Li and Be and the $^2$D state of N, the splittings are smaller than 1 cm$^{-1}$, so percentage errors are exaggerated. The $^3P_2$–$^3P_1$ splitting of the lowest $^3$P state in Te and Po is adequately reproduced, but not the corresponding $^3P_1$–$^3P_0$ splitting. Experimental results show that $^3P_0$ is lower in energy than $^3P_1$, namely the energetic level order is irregular: $^3P_2$, $^3P_0$ and $^3P_1$, rather than the inverted order $^3P_2$, $^3P_1$, and $^3P_0$ observed for O, S and Se. As was found in the later work by Koseki (unpublished), the origin of the incorrect order in the calculations lies in the omission of $^1S_0$ and $^1D_2$ states that are sufficiently close to interact with $^3P_0$ and $^3P_2$ respectively. By including these states the

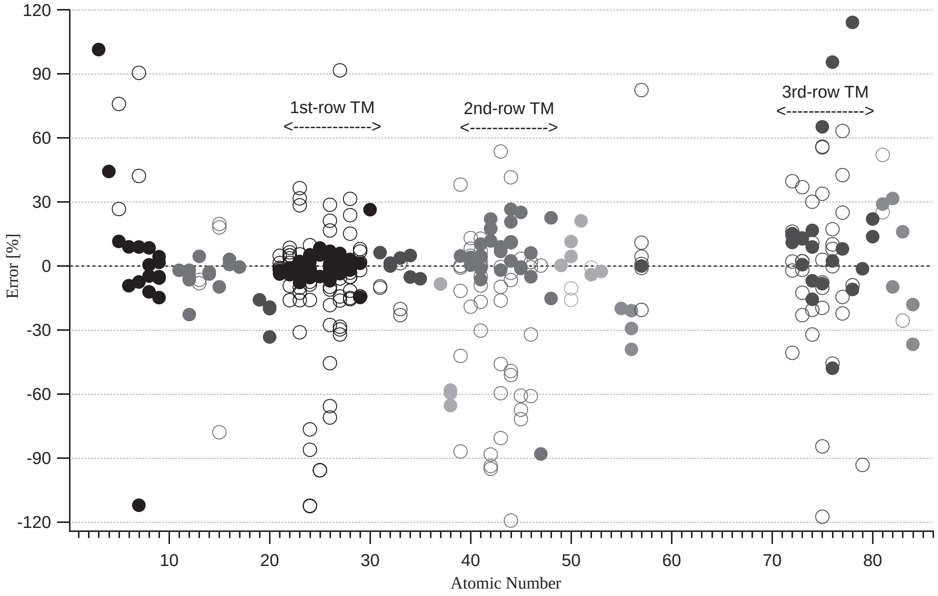

Figure 2. Percentage difference between the calculated energy splittings and the corresponding experimental ones. Positive and negative values indicate that the calculated splittings are overestimated and underestimated respectively. Closed circles: the lowest electronic states whose azimuthal quantum number *L* is non-zero. Open circles: higher electronically excited states.

experimental order was reproduced. For main group elements, 66% of the atomic energy splittings are predicted within 20% of the experimental values, and 83% of the calculated values are within 40% of the experimental values. Koseki *et al.* (1995) reported that, for 92 electronic states of non-hydride main group diatomic molecules, excluding alkali earth elements, only 11 states are in error by more than 30%. The parameters given in the table for alkali earth elements are not recommended for use owing to some large errors for these elements.

Unfortunately, few experimental data on diatomic transition metal hydrides are available (Huber and Herzberg 1979), so atomic spectral terms compiled by Moore (1949, 1952, 1958) were employed to determine effective nuclear charges for transition elements (Koseki *et al.* 1998). The $Z_{\text{eff}}$ parameters for transition elements are listed in Table 4. Their usefulness can be assessed by obtaining the SO splitting of 98 low lying atomic states (48 are from the first row, 26 from the second row and 24 from the third row). As mentioned above, even though the 3d SBKJC orbitals are qualitatively similar to correct 3d atomic orbitals, 4d and 5d SBKJC orbitals are nodeless, and, as a result, large $Z_{\text{eff}}$ values are given to the second- and third-row transition metals. The errors in the calculated splittings are plotted in figure 2. Even though serious errors are observed for Os, Ir and Pt, 70% of the energy splittings are predicted to be within 20% of the experimental values, and 81% are within 40% of the experimental values. This is surprisingly similar accuracy to the main group elements. The group 12 elements Zn, Cd and Hg have filled d orbitals, and, since their chemistry is dominated by sp rather than d orbitals, their $Z_{\text{eff}}$ values for such states are best determined as if they are main group elements; namely, the pseudo-orbitals for $(n+1)$sp determine the $Z_{\text{eff}}$. The same strategy should be used for the determination of $Z_{\text{eff}}$ for those low lying excited states of group 11 elements that do not involve open-shell d electrons.

Koseki *et al.* (1998) examined the larger errors found for transition elements, in some cases suggesting that the valence $(n+1)$p orbital needed to be included in the active space to improve results. The most serious errors in the predicted order of energy levels were observed in Os, Ir and Pt. This prompted an additional study (Koseki *et al.* 2001a) comparing the $Z_{\text{eff}}$–ECP approach with the full computation of $H^{\text{SO}}$, together with use of the RESC approximation for including $H^{\text{MV}}$ and $H^{\text{D}}$, and using all electron basis sets. In addition, for some cases, the effect of including additional electron correlation by means of singles and doubles CI was considered. Unfortunately, this was limited for technical reasons to only a subset of the external orbitals (those above the $n$d and $(n+1)$sp). Results for Re and Os were improved, but Ir and Pt remained unsatisfactory, although the all electron calculations suggested additional inclusion of electron correlation might give better results. It is clear that the third-row transition metal Ir represents a severe challenge to the hope that *LS*-coupled states may be treated with $H^{\text{SO}}$ as a perturbation, and perhaps this atom will require full Dirac–Coulomb–Breit computations to reproduce its spectra.

In summary, the $Z_{\text{eff}}$ approximation using ECP basis sets gives qualitatively accurate predictions for a majority of the SO splittings in atoms, even though errors greater than 30% sometimes appear. The applicability of this method to molecules also seems to be viable. In the late 1960s when the $Z_{\text{eff}}$ approach was first being popularized, the work of Walker and Richards (e.g. Walker and Richards 1968), which neglected only the two-centre, two-electron terms of $H^{\text{SO}}$ in diatomic molecules, indicated the difficulty of achieving quantitative accuracy with this procedure. Today, one has the ability to compute the two-electron term exactly, or to quite

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reasonable accuracy by judicious approximations described in the next section. Therefore, while this semiquantitative approach is the method of choice for moderate to large molecular systems, the more accurate and less empirical approaches are viable alternatives for atoms and small molecules.

### 2.5. *Comparative studies of one- and two-electron contributions*

In practice, bra and ket states are very often represented by linear combinations of either Slater determinants or configuration state functions (CSFs). CSFs can also be represented by linear combination of Slater determinants. Working in a CSF basis has the advantage of having a definite $S^2$ value; however, matrix element algebra becomes quite complex. Two different approaches are possible: a direct approach that is based on using Slater rules for a matrix element between two determinants and an indirect approach (Furlani and King 1985) based on evaluation of a generalized density factor (form factor) that multiplies either a one- or two-electron SOC integral.

The advantage of the indirect method is that it does not require storing the 2e integrals that are usually kept in memory in the direct method. The penalty for this advantage is having to calculate, sort and store the form factors. This effectively restricts the practical applicability of the indirect approach to the CAS type of wavefunction. Thus, the indirect method is best used with small active spaces and large basis sets, whereas the direct approach may not be able to handle large basis sets owing to limited computer memory. A determinant approach by Sjøvoll *et al.* (1997) could be classified as indirect in the terminology of this paper. This approach provides a considerable advantage over the previously existing form factor method briefly discussed below, as it provides the means of effectively calculating the generalized density factors without having to sort them. An intermediate method also exists, known as the symbolic matrix element method (Yarkony 1986), wherein the CSFs are divided into classes according to occupation schemes, and each scheme is then treated with the indirect approach.

It may be desirable for the molecular orbitals (MOs) used to construct the bra and ket to be different, in case these two states have different physical natures for example, one might be a Rydberg state and another a valence state. In this case, the two sets of orbitals can be made biorthogonal. The use of such corresponding orbitals (King *et al.* 1967) with identical core orbitals (doubly occupied space in all configurations) does not appreciably complicate matrix element evaluation for the case of CASSCF (or full CI, FCI) wavefunctions (Lengsfield *et al.* 1981). It is possible to use two separately and fully optimized orbital sets for the RAS SCF (RASSCF) generalization of CASSCF without too much extra work (Malmqvist and Roos 1989), again using biorthogonal orbitals. General CI states should be limited to a common set of orbitals in order to avoid the great increase in time needed to deal with non-orthogonal orbitals.

The Breit–Pauli SOC defined in equation (5) contains one- and two-electron terms. In most cases, the contributions due to the one- and two-electron SOC have opposite sign. An exception was found by Fedorov *et al.* (2001a) in the A $^2\Pi_u$ state of $O_2^+$, where both contributions are small and there is a region of the internuclear distance in which both have the same sign. In addition, because of the local nature of the operator and the explicit dependence of the one-electron operator (1E) on the nuclear charges, the one-electron contribution to SOC tends to grow rapidly with the nuclear charge, whereas the two-electron part (2E) grows much more slowly, owing

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to increased electron density in the regions close to the nuclei. The computational expense of evaluating these two operators is considerably different, by one order of magnitude. As discussed in the previous section, the $Z_{\mathrm{eff}}$ approach permits skipping the 2E term entirely, but the introduction of these parameters does not permit quantitative accuracy to be obtained. Nonetheless, the cost of evaluating the 2E term exactly has motivated the development of approaches wherein the 2E term is approximated. One such method is the mean field approximation of Hess *et al.* (1996), in which all multicentre two-electron integral terms are omitted.

By neglecting the most time-consuming active–active two-electron contribution, one obtains all of the one-electron and most of the two-electron contributions. This method is known as the partial two-electron method (P2E). Here only the basic idea is summarized, as the explicit formulae for all contributions can be found in Fedorov and Gordon (2000). A matrix element of the two-electron part of the SOC Hamiltonian between two Slater determinants $I$ and $J$ differing by two spin-orbitals $\mu$ and $\nu$ can be written as:

$$\langle I(\mu)|H^{2e}_{\mathrm{SO}}|J(\nu)\rangle = \sum_{\sigma=1}^{N} \big(\langle\sigma\mu|h^{2e}_{\mathrm{SO}}|\sigma\nu\rangle + \langle\mu\sigma|h^{2e}_{\mathrm{SO}}|\nu\sigma\rangle$$

$$-\langle\sigma\mu|h^{2e}_{\mathrm{SO}}|\nu\sigma\rangle - \langle\mu\sigma|h^{2e}_{\mathrm{SO}}|\sigma\nu\rangle\big), \tag{20}$$

where the sum runs over all $N$ electrons (occupied spin-orbitals). Note that there are two terms for both Coulomb-like and exchange-like terms. This comes from the fact that the two-particle SOC Hamiltonian $H^{\mathrm{SO}}$ does not possess permutation symmetry between particles 1 and 2, unlike the Coulomb operator. The first Coulomb-like term vanishes for real-valued orbitals, owing to the differential operator over the coordinates of electron 1 (that appears with $\sigma$ as bra and ket) in $h^{2e}_{\mathrm{SO}}$ (compare $\langle f|\nabla|f\rangle = -\langle f|\nabla|f\rangle^* = 0$ for real-valued functions $f$). The sum over all electrons consists of two parts, over core orbitals and over active orbitals. The former is retained in the P2E contribution, and can be efficiently summed algebraically, since the occupation number of each core orbital is 2 (during the summation the spin integration is also performed, reducing the matrix element to orbitals). Similar formulae can be derived for the case of determinants $I$ and $J$, which are identical or differ by two orbitals. P2E omits the considerably more expensive sum over active orbitals.

The partial two-electron method in practice requires little more resources than the one-electron method, for the following reasons:

(1) the number of determinant pairs to be considered is the same as for the one-electron method (at most one discoincidence allowed);
(2) the four-index integral transformation can be done with the expense of a two-index transformation;
(3) there is no need to store four-index two-electron integrals in the MO basis in memory.

Additional expenses include having to calculate two-electron integrals in the atomic orbital basis. These can be stored on disk while being calculated and read while doing the four-index transformation. This does not require a noticeable amount of memory, although, if available, larger buffers can be used to speed up

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the calculation. These expenses (integrals and transformation) are usually insignificant, especially when compared with the expense of the matrix element calculation for a large CI.

Several numerical examples (Fedorov and Gordon 2000) serve to illustrate the relative magnitudes of one- and two-electron terms and demonstrate that the partial method captures most of the full value of the SOC interaction.

Using a modified all electron basis set WTBS provided by Huzinaga and Miguel (1990) for X (X = C, Si, Ge, Sn, Pb) and cc-ptvz for H by Dunning (1989), the SOC between $^1A_1$ and $^3B_1$ states near their crossing was studied for a series of $XH_2$ molecules. The active space used here is [6/6], i.e. 6 electrons in 6 active orbitals. SO-CASCI SOC calculations were performed using biorthogonal orbitals with the core optimized for the singlet. The SO-MRCISD calculations were performed with singlet orbitals. The results obtained using the larger basis are given in table 5.

Note that at both levels of theory (CASCI, MRCISD), the agreement between P2E and 2E methods is quite reasonable for all group 14 elements, and the relative error decreases with increasing charge. The use of MRCISD has only a small effect relative to the CASCI results.

For $X_2^+$, X = O, S, Se, Te, SOC was studied at the SO-CASCI level at the CAS equilibrium geometry. The basis set was 6-21G (Binkley *et al.* 1980) (X = O) or 3-21G (Gordon *et al.* 1982, Dobbs and Hehre 1986) (X = S, Se, Te). The experimental value for the $^2\Pi_{3/2g}$–$^2\Pi_{1/2g}$ splitting in $O_2^+$ is 200.2 cm$^{-1}$ (Fedorov *et al.* 1999). The results are presented in table 6.

As for the $XH_2$ species, the partial two-electron method is seen to provide reasonable accuracy relative to the full 2E method. Tables 5 and 6 indicate that the first row of the periodic table, where the 1E term is less dominant, may require a full two-electron treatment if high accuracy is sought.

Table 5. $XH_2$ (X = C, Si, Ge, Sn, Pb) results[a] (WTBS basis set).

| | $M_{1e}$, CASCI | $M_{P2e}$, CASCI | $M_{2e}$, CASCI | $M_{1e}$, MRCISD | $M_{P2e}$, MRCISD | $M_{2e}$, MRCISD |
|---|---|---|---|---|---|---|
| $CH_2$ | 17.213 | 7.232 | 8.540 | 16.645 | 6.989 | 8.218 |
| $SiH_2$ | 52.50 | 11.54 | 12.12 | 51.13 | 11.24 | 11.79 |
| $GeH_2$ | 260.03 | 28.03 | 28.57 | 264.58 | 28.80 | 29.32 |
| $SnH_2$ | 575.47 | 40.18 | 40.56 | 601.18 | 42.85 | 43.23 |
| $PbH_2$ | 1479.22 | 65.60 | 65.92 | 1585.69 | 72.06 | 72.39 |

[a] $M_{1e}$, $M_{P2e}$, $M_{2e}$ denote absolute values of 1E, P2E and 2E matrix elements in cm$^{-1}$. The 1e and 2e matrix elements come with opposite sign.

Table 6. $X_2^+$ (X=O, S, Se, Te) CASCI/split basis results.

| | $R_{X\text{–}X}$ (Å) | $M_{1e}$ (cm$^{-1}$) | $M_{P2e}$ (cm$^{-1}$) | $M_{2e}$ (cm$^{-1}$) | $^2\Pi_{3/2g}$–$^2\Pi_{1/2g}$[a] (cm$^{-1}$) |
|---|---|---|---|---|---|
| $O_2^+$ | 1.267 | 125.70 | 42.98 | 47.76 | 155.9 |
| $S_2^+$ | 1.869 | 294.22 | 54.74 | 56.51 | 475.4 |
| $Se_2^+$ | 2.150 | 1039.36 | 107.85 | 109.24 | 1860 |
| $Te_2^+$ | 2.585 | 1869.04 | 135.16 | 136.05 | 3466 |

[a] $^2\Pi_{3/2g}$–$^2\Pi_{1/2g}$ splitting obtained with the full two-electron SOC, $2|M_{1e}$–$M_{2e}|$.

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Table 7. $BH_2$ and $AlH_2$ CASCI/MRCIS/MRCISD results.

| | | $BH_2$ | | | | $AlH_2$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| Level | Orbitals | $^2B_2$–$^2A_1$ (cm$^{-1}$) | $M_{1e}$ (cm$^{-1}$) | $M_{P2e}$ (cm$^{-1}$) | $M_{2e}$ (cm$^{-1}$) | $^2B_2$–$^2A_1$ (cm$^{-1}$) | $M_{1e}$ (cm$^{-1}$) | $M_{P2e}$ (cm$^{-1}$) | $M_{2e}$ (cm$^{-1}$) |
| CASCI | $^2A_1$c | 300.6 | 4.841 | 2.445 | 2.716 | 337.5 | 16.809 | 4.153 | 4.323 |
| | $^2B_2$c | −544.6 | 4.850 | 2.434 | 2.714 | 177.9 | 16.352 | 4.060 | 4.230 |
| | $^2A_1$ | 7578.5 | 4.949 | 2.493 | 2.792 | 8373.7 | 21.914 | 5.395 | 5.615 |
| | $^2B_2$ | −3852.7 | 5.064 | 2.546 | 2.841 | −5805.3 | 21.068 | 5.292 | 5.520 |
| | $^2A_1 + {}^2B_2$ | −1058.1 | 4.962 | 2.505 | 2.794 | 387.6 | 22.120 | 5.462 | 5.684 |
| MRSCI | $^2A_1$ | 578.5 | 4.726 | 2.380 | 2.661 | 1322.2 | 18.602 | 4.685 | 4.897 |
| | $^2B_2$ | −2962.9 | 4.776 | 2.394 | 2.671 | −1282.0 | 19.073 | 4.803 | 5.009 |
| | $^2A_1 + {}^2B_2$ | −2599.8 | 4.780 | 2.411 | 2.680 | 1357.9 | 19.836 | 4.960 | 5.168 |
| MRCISD | $^2A_1$ | 701.9 | 4.799 | 2.418 | 2.680 | 579.6 | 19.101 | 4.806 | 5.006 |
| | $^2B_2$ | −1499.7 | 4.815 | 2.412 | 2.680 | −411.7 | 18.705 | 4.733 | 4.933 |
| | $^2A_1 + {}^2B_2$ | −1160.9 | 4.797 | 2.417 | 2.677 | 38.2 | 19.529 | 4.897 | 5.097 |

'Orbitals' indicates the sets of molecular orbitals:

- $^2A_1$c: two separate MO sets, fully optimized for $^2A_1$, and $^2B_2$ optimized with $^2A_1$ core.
- $^2B_2$c: two separate MO sets, $^2B_2$ fully optimized, and $^2A_1$ using the $^2B_2$ core.

All other rows represent use of a single MO set, consisting of the state-averaged $^2A_1 + {}^2B_2$ (50% + 50%) orbital set.

$^2B_2$–$^2A_1$ refers to adiabatic separation between the two states.

SOC plays an important role in the chemistry of many high energy species, because it is very important for such materials to exhibit sufficiently high barriers to ensure stability. Such barriers can be greatly lowered as a result of potential energy curve crossing caused by diabatic interactions such as SOC. The SOC of $BH_2$ and $AlH_2$ was studied at the minimum energy crossing of the $^2A_1$ and $^2B_2$ surfaces. All valence electrons are included in the active space ([5/6]). The basis set for $BH_2$ is aug-cc-pVTZ (Dunning 1989) on both B and H, while for $AlH_2$ it is cc-pVTZ (Woon and Dunning 1993, Kendall *et al.* 1992) on Al and aug-cc-pVTZ on H. The effect of orbitals and CI level on both the separation between the $^2A_1$ and $^2B_2$ surfaces and the SOC with both full and partial two-electron methods can be seen in table 7.

The results for these molecules demonstrate the general trend that the choice of orbitals and CI level can have a dramatic impact on the splitting between the two adiabatic levels. Because two similar numbers are subtracted, high accuracy in both is required for an accurate difference. At the same time the SOC is not a property obtained as a difference and thus a much smaller effect of both orbitals and CI level is observed. Nonetheless, the SOC constants predicted by the P2E method are in good agreement with the much more resource-consuming full 2E method.

### 2.6. *Spin–orbit coupling with model core potentials*

Replacing some of the particle electrons by potentials is a very efficient tool in quantum chemistry. There are several types of potentials in use today, such as ECPs (Cundari *et al.* 1996), model core potentials (MCPs) (Klobukowski *et al.* 1999) and AIMPs (Seijo and Barandiaran 1999). The last two types of potentials are in principle capable of retaining the full, accurate nodal structure of the valence orbitals. On the other hand, it is well known that ECPs do not retain proper nodal structure and thus are not very efficient for computing SOC directly. Nonetheless, several methods are available: the effective charge approach (section 2.4), effective one-electron SO ECPs generated along with spin-free ECPs (Pacios and Christiansen 1985) or calculating the SO integrals in an all electron basis set and transforming them to be used with ECPs (Marian and Wahlgren 1996). Similar methods exist for AIMPs (Seijo 1995).

As shown in section 2.5, a matrix element of the SOC Hamiltonian between a pair of Slater determinants has three contributions: one electron (active–active), two electron (core–active) and two electron (active–active). In the case of MCPs, the active–active contributions can be computed in exactly the same way as for the AE case. However, core–active contributions are split into two parts, as there are two types of core orbitals: (a) the outer core orbitals that are explicitly kept in the MCP calculations (filled valence or semi-core orbitals ) and (b) the core orbitals that were replaced by a potential (MCP core). It is the latter type that that contributes most to the two-electron SOC.The MCPs explicitly include core orbitals in the definition of the potential itself, via the projection operator (Klobukowski *et al.* 1999); therefore, these exact atomic core orbitals may be utilized to obtain the major part of the core–active two-electron SOC (in fact, of the total two-electron SOC). Thus the core–active terms split into 'valence core–active' and 'MCP core–active'. Explicit formulae for the former term are given by Fedorov and Gordon (2000) and for the latter term by Fedorov and Klobukowski (2002). The partial two-electron method can be used, neglecting two-electron active–active contributions. Then one has to compute effectively a one-electron SOC, containing the active–active one-electron and core–active two-electron terms summed over the doubly occupied core. The two-electron terms are obtained from the MCP core and valence orbitals directly, without need for either transformation of the all electron integrals or using effective charges, as the MCP orbitals provide very good nodal structure and $\langle r^n \rangle$ expectation values. In order to improve the efficiency of the calculations, a one-centre approximation can be employed; it works very well in general as assessed by Walker and Richards (1970) and may be expected to work even better for the MCP core orbitals that are atomic like. High atomic symmetry (enforced by keeping only one-centre integrals) makes the computation of SOC integrals very efficient, as one-electron SOC integrals $A_{\mu\nu}$ are zero by symmetry if

(a) both $\mu$ and $\nu$ are s functions,
(b) $\mu$ or $\nu$ are of different parity and
(c) angular momenta of $\mu$ and $\nu$ differ by more than unity

As a consequence of (a), (b) and (c), the integrals also vanish when either $\mu$ or $\nu$ is an s function, and as a consequence of (b) and (c) the same is true whenever $\mu$ and $\nu$ have different angular momenta.

To demonstrate that the MCP SOC very well reproduces all electron SOC, some results by Fedorov and Klobukowski (2002) are presented in table 8. These calculations present an extension of the previously published study of one-electron SOC by Krause and Klobukowski (1996). The MCPs used remove all core electrons and the number of non-core atomic orbitals in the all electron and MCP cases are

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Table 8. SO splittings in $cm^{-1}$ for atoms (X), hydrides (XH) and diatomics ($X_2^+$) (X=P, As, Sb). Theoretical values were obtained within one-centre and partial two-electron approximations. Uncertain experimental values are given in parentheses.

| | Splitting | Method | P | As | Sb |
|---|---|---|---|---|---|
| X | $^2D_{3/2u}$ and $^2D_{5/2u}$ | SO-MCQDPT/AE | 13.32 | 254.1 | 1064.2 |
| X | $^2D_{3/2u}$ and $^2D_{5/2u}$ | SO-MCQDPT/MCP | 12.91 | 251.2 | 1079.4 |
| X | $^2D_{3/2u}$ and $^2D_{5/2u}$ | Experiment[a] | 15.61 | 322.1 | 1342.0 |
| XH | $0^+(^3\Sigma^-)$ and $1(^3\Sigma^-)$ | SO-MCQDPT/AE | 2.883 | 81.43 | 421.4 |
| XH | $0^+(^3\Sigma^-)$ and $1(^3\Sigma^-)$ | SO-MCQDPT/MCP | 3.023 | 81.39 | 423.2 |
| XH | $0^+(^3\Sigma^-)$ and $1(^3\Sigma^-)$ | Experiment[b] | | 117.6–118 | 655–660 |
| $X_2^+$ | $^2\Pi_{1/2u}$ and $^2\Pi_{3/2u}$ | SO-MCQDPT/AE | 227.6 | 1162.2 | 2449.3 |
| $X_2^+$ | $^2\Pi_{1/2u}$ and $^2\Pi_{3/2u}$ | SO-MCQDPT/MCP | 229.7 | 1158.3 | 2464.3 |
| $X_2^+$ | $^2\Pi_{1/2u}$ and $^2\Pi_{3/2u}$ | Experiment[c] | (260) | | |

[a] Moore (1949)
[b] Lindgren (1975), Dixon and Lamberton (1968), Bollmark and Lindgren (1974).
[c] Huber and Herzberg (1979).

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exactly the same. The matrix elements are those for the largest $M_S$ values of the corresponding multiplicities, and the imaginary unit i is omitted.

In calculations on atoms X (X = P, As and Sb), the active space consisted of four orbitals (s and p), and the $^2P_u$, $^2D_u$ and $^4S_u$ states were coupled by SO-MCQDPT (a method to be described in section 2.7). In the calculations of the corresponding hydrides XH (at the experimental geometry) the active space consisted of five orbitals (s and p on X and s on H), and their $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ states were coupled using SO-MCQDPT. In calculations of diatomic molecular ions $X_2^+$ (at the CASSCF optimized geometry) the active space consisted of eight orbitals (s and p on X) and only the $^2\Pi_u$ state was included in SO-MCQDPT. The one-centre approximation to both one- and two-electron SOC integrals as well as the partial two-electron method (P2E) are used throughout.

The slightly larger relative discrepancy in the case of XH comes in part from the fact that the splitting is a result of coupling between the $^3\Sigma^-$ and other states so the accuracy of the separation between the adiabatic states comes into play. Both sets of computational results differ from the experimental values; undoubtedly better polarization space and the explicit treatment of the scalar relativistic effects which were omitted to facilitate comparison between the all electron and MCP results may improve the agreement.

### 2.7. *Dynamic correlation and spin–orbit coupling*

Electron correlation can affect SOC coupling in several ways. Firstly, SOC is zero for single configuration real-valued wavefunctions, so one can say that the SOC interaction arises only when electron correlation is included (assuming an approach where SOC is not included in the SCF process). Secondly, electron correlation affects the spacing of the '*LS*' levels, namely the diagonal of the SOC matrix, and thus can shift its eigenvalues. Very often this is the major effect of dynamic correlation on SOC. Thirdly, electron correlation has a direct effect on the off-diagonal SOC matrix elements. In most cases, however, this direct effect of dynamic correlation is small, owing to the local (atomic-like) nature of the SOC interaction that makes contributions from chemically active (that is, those having fractional occupations) orbitals rather small. The major part of the direct dynamic electron, correlation effect on SOC usually comes from core correlation and, to a smaller degree, the one-electron active orbital contribution. Most basis sets are developed by focusing on the valence electrons, and most correlation methods are designed to recover the valence correlation. Thus accurate calculations of SOC may require basis sets suitable for core correlation. Nicklass *et al.* (2000) did a careful study of basis set effects on SOC in halogens.

Spin-free dynamic correlation effects contribute to the total energy, and, if only one state is considered, they do not affect, for example, the splitting between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ components of a $^2\Pi$ state (they are relevant to determining the minimum energy geometry, however). In contrast, dynamic correlation effects due to SOC directly affect the splitting.

In some cases dynamic correlation dramatically changes the active one- and two-electron contributions. An example was found by Fedorov *et al.* (2002) where the SOC interaction in $O_2^+$ was very sensitive to the electron correlation level, with CASCI, MRCIS, truncated, contracted and full MRCISD giving very different answers. Only CASCI and the full MRCISD (Fedorov, unpublished results) gave very good agreement with experiment, the former because of fortuitous error cancellation. It can be expected that for very heavy atoms electron correlation does have a large direct effect on SOC, through core correlation and the large magnitude of the SOC interaction. Usually, however, dynamic correlation has a relatively small effect on SOC, provided that near degeneracy ('non-dynamic') correlation (at the CASSCF level) is properly accounted for. Numerical examples are given in section 2.5 in tables 5 and 7. It is interesting to observe that the dynamic correlation effect on SOC in table 5 (comparing $M_{1e}$ for CASCI and MRCISD) varies from 3.4% (C), 2.7% (Si), 1.7% (Ge), 4.3% (Sn) to 6.7% (Pb), going through a minimum at Ge, consistent with the above general arguments.

The indirect effect of electron correlation through the '*LS*' term splittings is usually very important. A recently developed method, SO-MCQDPT (Fedorov and Finley 2001) efficiently incorporates all of the above-described effects of dynamic correlation. Through appropriately made approximations (treating the two-electron SOC only at the CASCI level and keeping only terms linear in SOC), it is possible to compute SOC having to deal with only one- and two-body terms in the perturbation treatment. Thus the spin-dependent part becomes much less resource demanding compared with the spin-free MCQDPT. In the recent work by Fedorov *et al.* (2003), SO-MCQDPT was successfully applied to U and UF that have complicated spectra because of partially filled f shells.

As illustrated by applications presented in section 3, SO-MCQDPT is capable of handling quite large systems. For systems containing a large number of nearly degenerate states, such as heavy atoms, one usually includes a few more states than one is primarily interested in. This forms a 'buffer' zone allowing the states of primary interest to interact with all important buffer states, which neglects only the effect of the even higher states omitted on the buffer states. The complicated spectrum of the Os atom was described with an average accuracy of about 1000 cm$^{-1}$ for most of the states presented in table 9, except for the highest ones, because of the limited number of states included into SO-MCQDPT.

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Table 9. Low lying levels of Os atom, in $\mathrm{cm}^{-1}$.

| $J$ | Label | SO-MCQDPT | Experiment[a] |
|---|---|---|---|
| 4 | $a^5D$ | 0 | 0 |
| 2 | $a^5D$ | 2743.8 | 2740.49 |
| 3 | $a^5D$ | 4098.4 | 4159.32 |
| 5 | $a^5F$ | 6238.1 | 5143.92 |
| 1 | $a^5D$ | 5894.2 | 5766.14 |
| 0 | $a^5D$ | 6657.4 | 6092.79 |
| 4 | $a^5F$ | 9810.7 | 8742.83 |
| 2 | $a^5F$ | 11635.7 | 10165.98 |
| 4 | $a^3F$ | 13185.6 | 11030.58 |
| 3 | $a^5F$ | 12494.5 | 11378.00 |
| 2 | $a^3F$ | 14347.9 | 12774.38 |
| 1 | $a^5F$ | 15160.1 | 13020.07 |

[a] Moore (1949).

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## 3. Applications

### 3.1. *Diatomic molecules*

Main group monohydrides were employed to fit the effective nuclear charges for main group elements, at the MCSCF/SBKJC(d,p) level of theory (Koseki *et al.* 1995). The percentage differences from experiment of the SO splittings in their lowest $^2\Pi$ and $^3\Pi$ states are plotted in figure 3. The $^2\Pi$ state is split into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels, and its SO constant is defined as the energy gap between these substates, where the $z$ components of the total angular momentum $\Omega$ are 1/2 and 3/2 respectively. Similarly, the levels $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$, are produced from the $^3\Pi$ state. In this case, the energy gaps between $^3\Pi_0$ and $^3\Pi_1$ and between $^3\Pi_1$ and $^3\Pi_2$ are defined as the SO constants. These two are the same value if only the original $^3\Pi$ state is included in an SO computation, but interactions with other electronic states make these two gaps slightly different and also lead to a slight splitting of the $^3\Pi_0$ into two substates, $^3\Pi_{0^+}$ and $^3\Pi_{0^-}$ ($\Lambda$ doubling). In figure 3, the average values of the energy gaps are used to derive the percentage differences.

The calculated results for hydrides of group 13–17 elements agree with the experimental data to within 20%. The fitting to experimental data consisted of linear relationships of the form $Z_{\text{eff}}=f_m Z$, with different constants used for each row $m$ in determining the scaling factor $f_m = a_m + b_m n$, where $n$ is the number of valence electrons and $b_m$ is very small compared with $a_m$. Since the same scale factor $f_m$ is used for an entire row, the fit for any one element is not exact. Of course, the good agreement with experiment should be ascribed to these monohydrides being used to determine the $Z_{\text{eff}}$ values. Unfortunately, errors of more than 50% are observed for alkali earth hydrides. Alkali earth elements have closed-shell $n$s orbitals, so that the lowest $^2\Pi$ state of their hydrides is an electronically excited state. No experimental datum has been found so far for excited states of alkali monohydrides and/or their anions. Therefore, in figure 3, the $Z_{\text{eff}}$ results for alkali hydrides are compared with all electron results obtained using the RESC approximation and the full Breit–Pauli Hamiltonian in the SOC calculations, excluding LiH anion because of the quite small splitting in its lowest $^2\Pi$ state. The $Z_{\text{eff}}$ approximation apparently underestimates the splittings in alkali hydrides and/or their anions. Such a discrepancy in alkali and alkali earth hydrides suggest that extensive effects of

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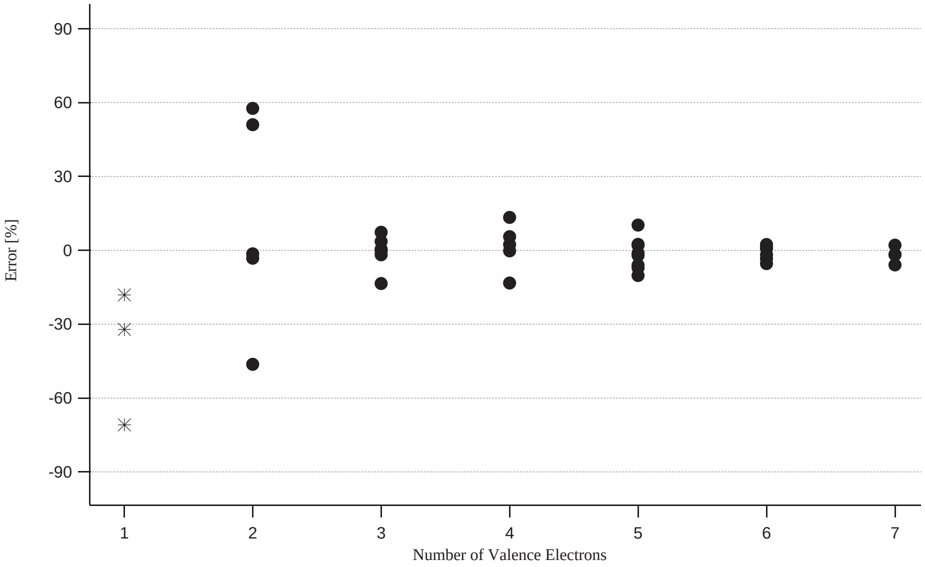

Figure 3. Percentage difference between the calculated energy splittings and the corresponding experimental ones in main group monohydrides, as a function of the number of valence electrons ($n$) on the main group atom, e.g. $n = 2$ corresponds to Be–Ba hydrides.

dynamic correlation should be considered in electronically excited states of molecules. In fact, the second-order CI wavefunctions give slightly better results for the $\Pi$ states in alkali and alkali earth hydrides (Koseki, unpublished).

Koseki *et al.* (1995) used the $Z_{\text{eff}}$ values determined to fit monohydride experimental data for many ground and excited states of non-hydride diatomics. As shown in figure 4, an error of less than 30% is observed in 92 of 106 states (85%), although a few (not shown in the figure), especially electronically excited states, have an error larger than 100%. Excluding the alkali earths, only 11 electronic states out of 96 considered have errors greater than 10%. The larger errors occurred for $C_2^+$, AlS, SeC, AlI, GaI, InI, $Br_2$, MgCl, $TeO^+$, TeCl and TeBr, and Koseki *et al.* (1995) discussed possible sources and solutions for these cases with larger errors. Thus, as long as energetically low lying states are considered, the $Z_{\text{eff}}$ approximation is applicable to the investigation of SO effects in molecules in a qualitative manner.

Koseki *et al.* (2001b) recently reported the relativistic potential energy curves of Group 4 hydrides, namely TiH, ZrH and HfH. Two methods of calculation were employed in this investigation: one is the $Z_{\text{eff}}$ method in which second-order CI based on MCSCF orbitals using SBKJC(f,p) basis sets is used to construct SOC matrices. The other method employs an all electron basis set MIDI (Huzinaga *et al.* 1984), augmented by three sets of p functions for the both transition element and hydrogen and by one set of f functions for transition element, instead of the SBKJC(f,p) basis set. In this second approach the RESC approximation is also used and the full Breit–Pauli Hamiltonian is employed in the construction of SO matrix elements. This method is referred to as 'AE' in the following discussion. The AE results were used as reference data for discussing the applicability of the $Z_{\text{eff}}$ approximation.

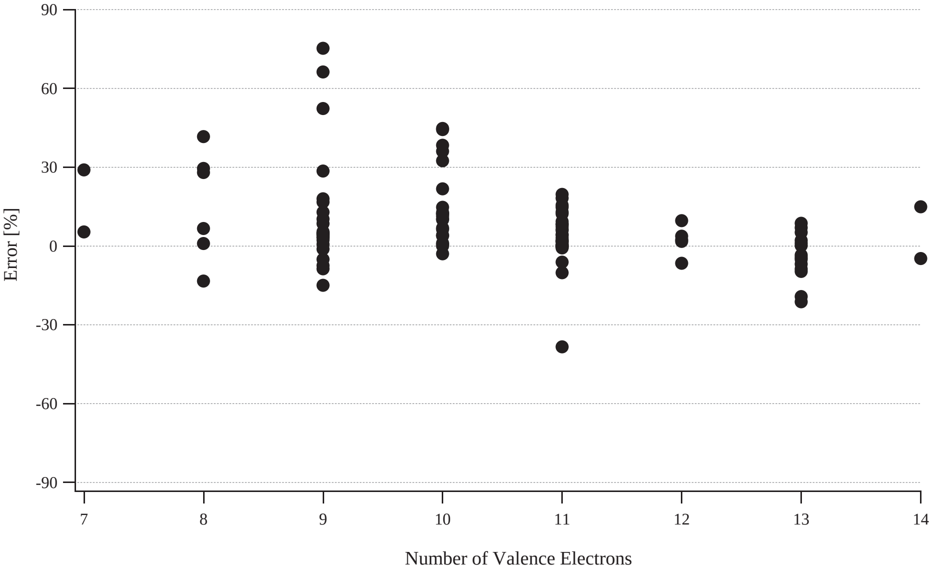

Figure 4. Percentage difference between the calculated energy splittings and the corresponding experimental ones in main group diatomic molecules (non-hydrides).

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Koseki *et al.* (2003) have just finished similar calculations of relativistic potential energy curves of group 3 and 5 hydrides: ScH, YH, LaH and VH, NbH, TaH. In both sets of calculations, the MCSCF active space includes the *n*d and (*n*+1)sp orbitals of the transition elements and the 1s orbital of hydrogen, and the second-order CI includes single and double excitations into all external orbitals in the group 3 and 4 hydrides and the lowest 13 external orbitals in the group 5 hydrides in order to keep computations practical. Table 10 summarizes the dissociation energies, equilibrium internuclear distances, vibrational frequencies, anharmonicities and rotational constants of the ground states in these hydrides.

The ground state in the group 3 hydrides (ScH, YH and LaH) is $^1\Sigma^+$ without SOC effects. The SOC of this state leads to only one level $^1\Sigma_0^+$ ($\Omega=0^+$), and since there is no other state close in energy, it remains the ground state. The $Z_{\text{eff}}$ dissociation energies included in Table 10 are 10–20% smaller than the corresponding AE ones, but the equilibrium internuclear distances are in good agreement with each other, as well as with available RECP results (Balasubramanian 1997). Since the MIDI basis set is unavailable for the La atom, only the $Z_{\text{eff}}$ calculation has been performed for LaH. The $Z_{\text{eff}}$ equilibrium distance of LaH is in good agreement with the relativistic MP2 results (Laerdahl *et al.* 1998) and experiment (Ram and Bernath 1996a).

Turning to group 4, both the $Z_{\text{eff}}$ and the AE results show that TiH and ZrH have $^4\Phi$ and $^2\Delta$ as their ground states without SOC effects respectively but that these two states are close together (Koseki *et al.* 2001b). On the other hand, HfH definitely has $^2\Delta$ as its ground state. When the SOC effects are considered, a $^4\Phi$ state is split into four doubly degenerate levels, $^4\Phi_{3/2}$, $^4\Phi_{5/2}$, $^4\Phi_{7/2}$ and $^4\Phi_{9/2}$, while the doubly degenerate levels $^2\Delta_{3/2}$ and $^2\Delta_{5/2}$ originate from the $^2\Delta$ state. The ground state is apparently $^2\Delta_{3/2}$ in HfH and $^4\Phi_{3/2}$ in TiH. On the other hand, the $^2\Delta_{3/2}$ and $^4\Phi_{3/2}$ are close in energy to each other in ZrH, but our calculations show that the ground state

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Table 10. Dissociation energies, equilibrium internuclear distances, vibrational frequencies, anharmonicities and rotational constants of the ground states in group 3, 4 and 5 hydrides.

| Molecule | State | Method | $D_e$ | $R_e$ | $\omega_e$ | $\omega_e\chi_e$ | $B_e$ | $\mu$ |
|---|---|---|---|---|---|---|---|---|
| ScH | $\Omega=0$ | ECP | 15653 | 1.8029 | 1564 | 26.33 | 5.364 | 1.3337 |
| | | AE | 20596 | 1.8147 | 1549 | 15.78 | 5.281 | 1.0801 |
| | | Difference (%) | −24 | −1 | 1 | 67 | 2 | 23 |
| | | Experiment[a] | | 1.775 | 1547 | | | |
| YH | $\Omega=0$ | ECP | 21240 | 1.9574 | 1496 | 21.08 | 4.486 | 1.3338 |
| | | AE | 24387 | 1.9560 | 1491 | 16.94 | 4.490 | 1.2317 |
| | | Difference (%) | −13 | 0 | 0 | 24 | −0 | 8 |
| | | Experiment[b] | | 1.923 | 1530 | | | |
| LaH | $\Omega=0$ | ECP | 19316 | 2.0805 | 1428 | 21.02 | 3.956 | 2.244 |
| | | Experiment[c] | | 2.032 | | | | |
| TiH | $\Omega=3/2$ | ECP | 14390 | 1.8299 | 1505 | 25.40 | 5.201 | 2.0856 |
| | | AE | 15558 | 1.8162 | 1266 | −4.78 | 5.280 | 1.8674 |
| | | Difference (%) | −8 | 1 | 19 | | −1 | 12 |
| | | Experiment[d] | 15809 | | 1385 | | | |
| ZrH | $\Omega=3/2$ | ECP | 17352 | 1.8589 | 1635 | 34.84 | 4.988 | 0.8644 |
| | | AE | 19760 | 1.8599 | 1622 | 21.93 | 4.978 | 0.8841 |
| | | Difference (%) | −12 | −0 | 1 | 59 | 0 | −2 |
| HfH | $\Omega=3/2$ | ECP | 19284 | 1.8623 | 1646 | 25.64 | 4.935 | 0.7515 |
| | | AE | 23442 | 1.8688 | 1632 | 17.97 | 4.901 | 0.9001 |
| | | Difference (%) | −18 | −0 | 1 | 43 | 1 | −17 |
| | | Experiment[e] | | 1.831 | | | | |
| VH | $\Omega=0$ | ECP | 13967 | 1.7742 | 1629 | 31.21 | 5.576 | 1.7064 |
| | | AE | 14891 | 1.7830 | 1575 | 25.05 | 5.473 | 1.8124 |
| | | Difference (%) | −6 | −0 | 3 | 25 | 2 | −6 |
| | | Experiment[f] | 17173 | | | | | |
| NbH<br>Dsp | $\Omega=0$ | ECP | 18059 | 1.8221 | 1588 | 23.12 | 5.180 | 2.4694 |
| | | AE | 19616 | 1.8304 | 1568 | 19.52 | 5.107 | 2.3558 |
| | | Difference (%) | −8 | −0 | 1 | 18 | 1 | 5 |
| NbH<br>dsds | $\Omega=0$ | ECP | 18972 | 1.8372 | 1612 | 23.66 | 5.111 | 2.6786 |
| | | AE | 20676 | 1.8484 | 1513 | 14.67 | 5.025 | 2.5187 |
| | | Difference (%) | −8 | −1 | 7 | 61 | 2 | 6 |
| TaH | $\Omega=2$ | ECP | 16124 | 1.7798 | 1751 | 25.40 | 5.405 | 1.0369 |
| | | AE | 19846 | 1.7621 | 1671 | 11.38 | 5.513 | 1.2140 |
| | | Difference (%) | −19 | 1 | 5 | 123 | −2 | −15 |

[a] Ram and Bernath (1996b).
[b] Ram and Bernath (1994b).
[c] Ram and Bernath (1996a).
[d] $D_e$, Barone and Adamo (1997); $\omega_e$, Chertihin and Andrews (1994).
[e] Ram and Bernath (1994a).
[f] Barone and Adamo (1997).

in ZrH is $^2\Delta_{3/2}$ which has 93% $^2\Delta$ character, in agreement with several studies reported previously (see references in Koseki *et al.* (2001b)). At any rate, it is true that the ground state has $\Omega = 3/2$ for all group 4 hydrides, even though their Russell–Saunders designations are different. On the basis of these results, it can be said that the $Z_{\text{eff}}$ dissociation energies of the ground states are underestimated by about 3000–4000 cm$^{-1}$; the SBKJC basis set seems not flexible enough to provide a quantitatively correct description of the bonding character in these monohydrides. On the other hand, the AE method provides a rather good prediction of the dissociation energies (see references in Koseki *et al.* (2001b)). The equilibrium bond distances were overestimated using both methods by 0.01–0.02 Å in comparison with the previous theoretical and experimental results.

Next, consider the group 5 hydrides. The ground state at the equilibrium internuclear distance is predicted to be $^5\Delta$ in VH and NbH and $^3\Phi$ in TaH without the SOC effects. The $^5\Delta$ state is split into two non-degenerate levels, $^5\Delta_{0+}$ and $^5\Delta_{0-}$ (after $\Lambda$ doubling), and four doubly degenerate levels, $^5\Delta_1$, $^5\Delta_2$, $^5\Delta_3$ and $^5\Delta_4$ by SOC effects. As a result, the ground state is $^5\Delta_{0+}$ in VH and NbH in the relativistic scheme. In TaH, SOC should split the $^3\Phi$ state into $^3\Phi_2$, $^3\Phi_3$ and $^3\Phi_4$. Although the lowest $^5\Delta$ state is distinctly higher in energy than the lowest $^3\Phi$ state at both levels of computation without SOC, the introduction of the SOC effects leads to a small energy gap between the lowest $^3\Phi_2$ and $^5\Delta_{0+}$ states (321 ($Z_{\text{eff}}$) and 562 (AE) cm$^{-1}$), and thus we predict that the ground state is $^3\Phi_2$ by a small margin. Cheng and Balasubramanian (1991) also reported a small energy gap between these states (326 cm$^{-1}$), but they concluded that $^5\Delta_{0+}$ is lower in energy than $^3\Phi_2$. Calculations with improved accuracy are needed to settle this point. The $Z_{\text{eff}}$ dissociation energy of the ground state is smaller than the AE value by less than 10% in VH and NbH and by about 20% in TaH. The equilibrium internuclear distance and vibrational frequency are in good agreement with each other in all group 5 hydrides. The AE method reproduces the RECP (Cheng and Balasubramanian 1991) and model potential (Wittborn and Wahlgren 1995) results reported previously to within 10%.

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In the study of group 5 hydrides, one serious discrepancy appears in the dissociation limit: both $Z_{\text{eff}}$ and AE methods indicate that the ground state is $^4$F arising from a $(4d)^3(5s)^2$ configuration in all group 5 elements. However, according to Moore's experimental reports (1949, 1952, 1958), although the ground state is $^4$F in V and Ta atoms, in Nb it is $^6$D arising from the configuration $(4d)^4(5s)^1$. The energy difference between the lowest $^4F_{3/2}$ and $^6D_{1/2}$ states is reported experimentally as 1143 cm$^{-1}$, but this difference is computed to be $-440$ cm$^{-1}$ in our investigation (Koseki *et al.* 2003). This discrepancy in the dissociation limit of NbH can be removed by using an MCSCF active space which includes two sets of d and s orbitals for the transition element (with no active p orbital) and a 1s orbital of hydrogen. These results are labelled dsds in table 10 and suggest that radial d correlation may be quite important. The choice between including $(n+1)$p or $(n+1)$d orbitals on the transition metal in the active space is made the basis on of the competition between the importance of the correlation of the $n$d orbital and the coupling of the $(n+1)$p excited states. Nevertheless, the chemical properties of the ground state in NbH are reasonable at the equilibrium internuclear distance. The details of these results will be discussed in a forthcoming paper (Koseki *et al.* 2003)

Figure 5 plots the dissociation energies and equilibrium internuclear distances against the periodic row of transition elements in each transition row, where the AE values for LaH is assumed to be the same as the $Z_{\text{eff}}$ ones. The equilibrium internuclear distances of group 3 hydrides monotonically increase across the row, while those for group 4 are almost constant and no clear trend is observed for group 5. The behaviour of the group 5 hydrides could be explained by lanthanide

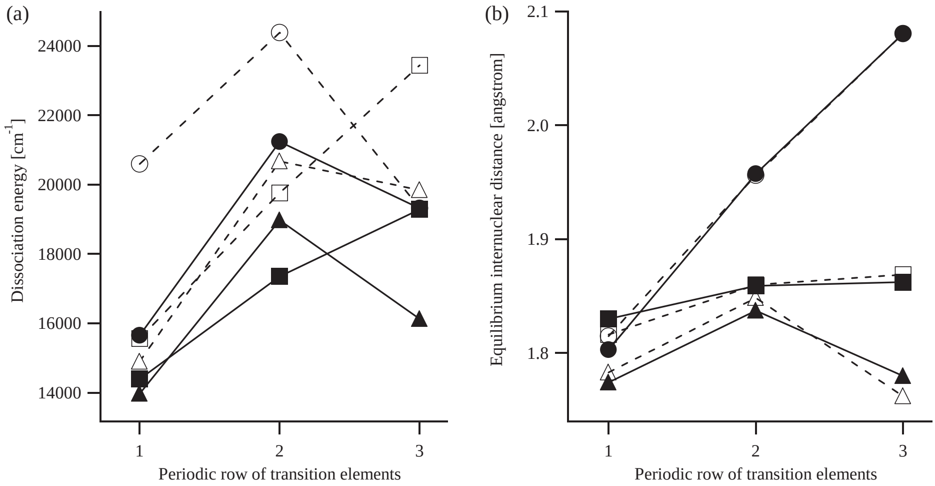

Figure 5. Comparison of (*a*) dissociation energies and (*b*) equilibrium internuclear distances. The full and broken lines are for the $Z_{\text{eff}}$ and all electron results respectively. Circles: group 3 hydrides. Squares: group 4 hydrides. Triangles: group 5 hydrides.

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contraction, since LaH has no 4f electron and 4f orbitals are completely filled in HfH and TaH. The dissociation energies have no obvious trend.

SOC plays an important role in some excited states of group 11 hydrides. These molecules are frequently used to illustrate scalar relativistic effects, and several papers provide examples. The hydrides of Ag and Au were extensively studied by Witek *et al.* (2000), and recently a paper describing an unusual potential curve of the first excited state of AgH was published by Witek *et al.* (2002). For these molecules the ground state is $^1\Sigma^+$ and the effects of SOC manifest themselves as avoided crossings of some excited states and as splitting of atomic-like states at large separation.

### 3.2. *Vibrational dependence of spin–orbit coupling constant in diatomics*

The SOC constant (SOCC) is usually defined for linear molecules (e.g. Hess *et al.* 1995) as

$$A_v = \frac{1}{\Lambda\Sigma}\left\langle \Psi^v_N \Psi_e \middle| H^{\text{SO}} \middle| \Psi^v_N \Psi_e \right\rangle, \tag{21}$$

where $\Lambda$ and $\Sigma$ are eigenvalues of $L_z$ and $S_z$ respectively; $v$ is the vibrational level and subscripts '$N$' and '$e$' denote nuclear and electronic parts of the wavefunction respectively (in the adiabatic approximation). The SOCC is an averaged measure of the SOC for a given adiabatic term. It reflects the dependence of the SOC splitting on the molecular geometry. Even for light molecules the SOCC varies significantly with distance, representing the change of molecular orbitals relative to atomic ones at the infinite separation.

In order to account for the coupling of several states, one can construct a Hamiltonian matrix in the basis of adiabatic states, including all interactions of interest into the Hamiltonian. In the case of SOC, one can construct the following matrix (Fedorov *et al.* 2001a): $\langle \Psi^v_N \Psi^i_e | \hat{H} | \Psi^{v'}_N \Psi^{i'}_e \rangle$, where $i$ and $i'$ denote adiabatic levels. If the potential energy surface is close to a Morse potential shape, which is often the case, then it is convenient to fit the surface to a Morse potential and obtain its eigenfunctions $\Psi_N^v$ analytically. Coupling between adiabatic levels can also be fitted to an appropriate function. While the exact shape for dependence of SOC on internuclear distance $R$, $A(R) \equiv \langle \Psi_e(R)|H_{\mathrm{SO}}|\Psi_e(R)\rangle$, is unknown, for the doublet and quartet $\Pi_u$ states of CO$^+$ and O$_2^+$ it was found by Fedorov *et al.* (1999, 2001a) to behave as $h\tanh[s(R-R_0)]+A_0$ and for the X$\,^2\Pi_g$ state of O$_2^+$ as $h\exp\left[-s(R-R_0)^2\right]+A_0$. Another approach is to compute the nuclear wavefunction and coupling on a grid and then to integrate over nuclear coordinates numerically. In this case the discrete variable representation (DVR) technique described in Witek *et al.* (2002) is very useful for accurate numerical computation of a wavefunction, given a potential.

Experimentally, the vibrational dependence of the SOCC is well known and data with accuracy on the order of 1 cm$^{-1}$ or better are available for many molecules. Coupling between vibrational levels is also observed experimentally and is seen as perturbations on the plots of the SOCC versus vibrational number $v$. The nature of such interactions can be understood with the help of theory. By diagonalizing the Hamiltonian in equation (21), one can easily determine what states cause sudden jumps in the SOCC. This, however, represents a rather challenging problem for *ab initio* methods, since the interactions are very small (for light molecules) and for a quantitatively correct analysis vibrational levels and their coupling should be accurate on the order of several cm$^{-1}$ or better. While the coupling can be obtained reasonably accurately at the present level of computational capabilities, the vibrational levels that come into play through the spin-free part of the Hamiltonian (which is diagonal in the basis of adiabatic levels) are a much more challenging problem.

For illustration, the SOCCs for several states in O$_2^+$ and CO$^+$ can be considered, following the study of A$\,^2\Pi_{3/2,1/2u}$ (CO$^+$), X$\,^2\Pi_{3/2,1/2g}$ (O$_2^+$) by Fedorov *et al.* (1999) and A$\,^2\Pi_{3/2,1/2u}$ (O$_2^+$), a$\,^4\Pi_{5/2,3/2,1/2,-1/2u}$ (O$_2^+$) by Fedorov *et al.* (2001a). The potential energy curves computed with the MRCISD method based on an all valence CAS (8 orbitals) agreed with experiment within 0.0005–0.005 Å in equilibrium distances, within 5–44 cm$^{-1}$ in harmonic and 0.15–2.4 cm$^{-1}$ in anharmonic frequencies.

SOCC plots are presented in figure 6. It can be seen that the shape of the dependence of the SOCC on the vibrational number is well reproduced for all cases studied. An approach based on single-point calculations at the experimentally determined averaged distances $R$ assigned to each level $v$ starts to depart from experiment for large values of $v$ (figures 6(*a*) and 6(*b*)). Unsatisfactory performance of this approach can be explained by much delocalized wavefunction $\Psi_N^v$ that does not correspond to the density equal to the Dirac delta function centred at $R_v$. This is caused by the increase in anharmonicity as the vibrational quantum number increases. Not much improvement is gained by using experimental values of Morse potential parameters (figures 6(*c*) and 6(*d*)). In the latter case, the agreement is quite good at the *ab initio* level and in the former case it is the values of $A(R)$ that need improvement. In the A$\,^2\Pi_u$ state SOC was found to be very sensitive to the level of electron correlation. The relatively low level results given by CAS agree with experiment quite well owing to error cancellation. Further improvement of electron correlation to MRCIS and contracted MRCISD levels actually made the agreement worse and only full uncontracted MRCISD was able to give accurate values.

Perturbations (sudden jumps) seen in figures 6(*a*), 6(*c*) and 6(*d*) are due to coupling to other states. Jumps occur if two vibrational levels are very close to each

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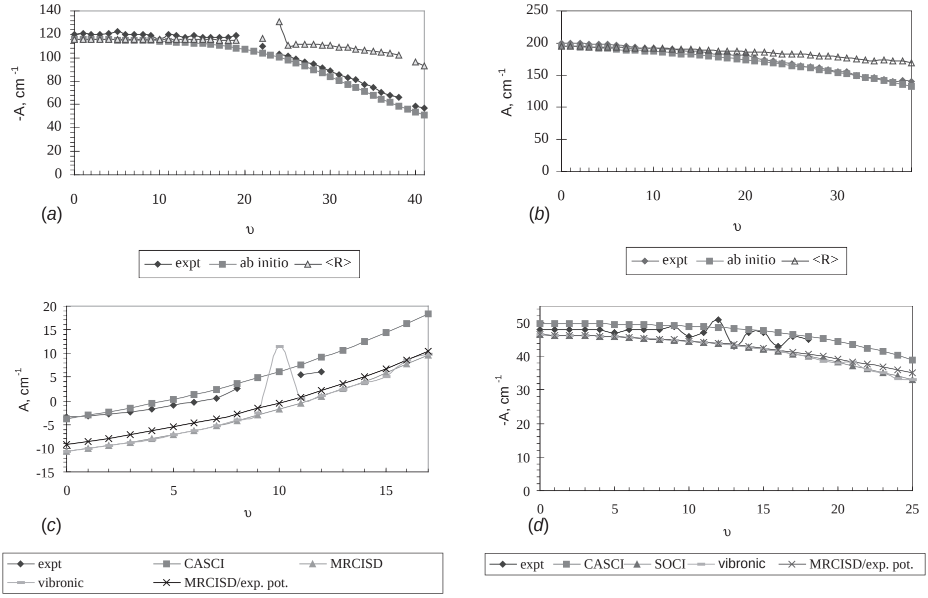

Figure 6. Vibrational dependence of SOCC in (*a*) $CO^+$ ($A\,^2\Pi$), (*b*) $O_2^+$ ($X\,^2\Pi_g$), (*c*) $O_2^+$ ($A\,^2\Pi_u$), (*d*) $O_2^+$ ($A\,^4\Pi_u$). '$\langle R\rangle$' refers to computing *ab initio* SOC at the geometry given by the experimental value of $\langle\Psi_\nu|R|\Psi_\nu\rangle$. 'MRCISD/exp. pot.' refers to using experimental values for the Morse potential with *ab initio* values of SOC. 'Vibronic' refers to the level coupling model, described in the text.

other (splitting is comparable with the interaction between the two). In the study by Fedorov *et al.* (2001a) such coupling of $A\,^2\Pi_u$, $a\,^4\Pi_u$ and $^2\Sigma_u^+$ in $O_2^+$ was conducted. The $^2\Sigma_u^+$ state crosses the other two and vibrational levels corresponding to the crossing point are perturbed. From both numerical and theoretical arguments it was demonstrated that experimentally seen perturbations in $A\,^2\Pi_u$, $a\,^4\Pi_u$ are due to the $^2\Sigma_u^+$ state. Quantitative theoretical predictions of the perturbed levels were not in good accord with experiment. Anharmonic frequencies are usually relatively more difficult to reproduce theoretically than harmonic frequencies; thus, the larger the vibrational number $\upsilon$, the greater the error in vibrational levels. For computations requiring such high accuracy (several $cm^{-1}$ or better), other minor interactions become important, such as spin–spin coupling and various effects of rotational movement. Using the adiabatic approximation itself can introduce a comparable error. Thus we see that while *ab initio* values of SOCCs are in good quantitative agreement with experiment, perturbations caused by other states are still a challenging problem.

### 3.3. *Spin–orbit coupling and non-adiabatic transitions in polyatomic molecules*

One of the important applications of SOC is to study non-adiabatic transitions. It is quite common for ground and especially excited state potential energy surfaces of molecules to cross. Such crossings, known as conical intersections (Yarkony 2001) can dramatically alter the stability of molecules owing to the possibility of crossing from one state to another. If such crossings are overlooked then low barrier transitions can be missed and an incorrect chemical picture will arise. The probability of transition can be computed with the semiclassical Landau–Zener model (Nakamura 1987), that is on the basis of the assumptions of linear diabatic

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terms and constant diabatic coupling. The matrix element that appears in the probability should properly take spin degeneracy into account. This is easily done using the normalized matrix element $C_{S,S'}$ between two states with $S$ and $S'$ ($S(S+1)$ are eigenvalues of $S^2$) introduced by Fedorov (1999). $C_{S'S'}$ is zero if $S$ and $S'$ differ by more than 1 and $C$ is symmetric, i.e. $C_{S,S'} = C_{S',S}$:

$$C_{S,S'} \equiv \sum_{M_S=-S}^{S} \sum_{M'_S=-S'}^{S'} \left| \left\langle SM_S \middle| \hat{H}^{\mathrm{SO}} \middle| S'M'_S \right\rangle \right|^2$$

$$= \frac{2\min(S,S')+1}{3} \left[ \left\langle S \middle| \hat{L}_x \middle| S' \right\rangle^2 + \left\langle S \middle| \hat{L}_y \middle| S' \right\rangle^2 + \left\langle S \middle| \hat{L}_z \middle| S' \right\rangle^2 \right] \tag{22}$$

The Landau–Zener probability of transition between two adiabatic levels $i$ and $j$ is given by

$$P(i,j) = 1 - e^{-2\delta_{ij}}, \quad \delta_{ij} = \pi \frac{|V_{ij}|^2}{\hbar v |g_i - g_j|} = \pi \frac{C_{S_i,S_j}}{(2\min(S_i,S_j)+1)\hbar v |g_i - g_j|} \tag{23}$$

where $g$ is the adiabatic energy gradient, $v$ is the velocity of the molecule at the transition point and $V_{ij}$ is a matrix element of a diabatic operator (SOC in this case) coupling two adiabatic states $i$ and $j$.

It should be noted that the non-adiabatic state crossing has seams of dimension $3N$-7 ($3N$-6 for linear molecules) and one is usually interested in the minimum energy crossing point. As an approximation to that point, one can follow the minimum energy path of the reaction, provided that the geometries of the two states that cross are not too different. The crossing in general does not possess the properties of a true transition state (a Hessian with only one imaginary frequency) and thus conventional transition state searches cannot be used directly.

Matsunaga *et al.* (1996) applied the $Z_{\mathrm{eff}}$ method to the main group triatomic molecules $XH_2$ (X = C, Si, Ge, Sn and Pb) in order to obtain the relativistic potential energy surfaces of the lowest singlet and triplet states. The simple one-dimensional Landau–Zerner approximation was used to estimate the transition probability of the ISC at the MEX point along the potential seam between these states. ISC occurs in $CH_2$ and $SiH_2$ only when the kinetic energy is relatively small, but the transition is accessible at any kinetic energy in $SnH_2$ and $PbH_2$ owing to the strong SOC and larger mass. $GeH_2$ belongs to an intermediate case.

In the study of the reaction of $Ti^+$ and ethane, Moc *et al.* (2000) found that the reaction starts off in the quartet state and proceeds through a non-adiabatic crossing to the doublet state through a number of intermediates and transition states to the final products ($TiC_2H_4^+H_2$), crossing back to quartet and then again to doublet at MCQDPT and CCSD(T) levels and there was only one initial crossing at the B3LYP level. This crossing reduced the value of the reaction barrier from 17.0 to 8.0 kcal mol$^{-1}$ (MCQDPT). The normalized matrix element was computed to be 50–55 cm$^{-1}$, depending on the method used, and the probability of transition was computed as a function of temperature. The value at room temperature is 13.4%.

Another application of SOC is to study how the energy levels are affected when SOC is included. In the study by Ajitha *et al.* (2002), alkyl and aryl iodide compounds that have been extensively studied experimentally were investigated using SO-MCQDPT. In those systems SOC creates two dissociation channels corresponding to the ground $^2P_{3/2u}$ and excited $^2P_{1/2u}$ states of the iodine atom.

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Thus SOC is the driving force that is behind the branching between the two states. Going from alkyl to aryl substituents as well as fluorination are of significant interest. In the SO-MCQDPT study the level structure had previously only been speculated on the basis of the available experimental data; it was placed on a firmer theoretical foundation by the *ab initio* calculations. Reliable experimental excitation energies available for $CH_3I$ and $CF_3I$ to several per cent; however, for much of the presented data there were no experimental data for comparison.

## 4. Conclusions

It is clear that SOC is ubiquitous among a very broad swath of chemistry physics and biochemistry and biology. The impact of SOC on chemical and physical properties includes the following:

- the quantum dynamics of atom–molecule and molecule–molecule reactions;
- the electronic structure of atoms and diatomic molecules, with increasing impact as the atomic number increases;
- the details of photoionization of small molecules as a function of vibrational quantum number;
- mechanisms of chemical reactions, especially for species with two or more low lying electronic states whose relative positions on the energy scale change as a function of reaction coordinate, a very common occurrence;
- the photochemistry and photobiology of polyatomic and biomolecules.

The ability to predict SCC and related properties reliably clearly depends on the availability and development of reliable methods. Especially over the past decade, several methods of varying sophistication have been developed. The degree to which these methods have been tested is limited, but some clear trends have emerged:

- The $Z_{\mathrm{eff}}$ method can provide qualitatively useful results, especially when adequate all electron basis sets are available. However, in general, the partial two-electron and similar methods are about as computationally efficient and more quantitatively reliable.
- A major deficiency is the general lack of adequate atomic basis sets. This includes all electron basis sets for the heavier elements core-correlated basis sets for most elements and valence basis sets for effective core potentials and model potentials. Because most properties of interest to chemists are primarily manifested in the valence region, most attention by basis set developers has logically focused on this region of space, with much less attention paid to the core region that is so critical to accurate predictions of SOC. Similarly, most ECPs and associated basis sets were developed before there was sufficient computer hardware to handle extended basis sets, so these ECP basis sets are generally much too small to provide accurate calculations.
- It is also clear that one needs both an adequate zero-order wavefunction and an adequate representation of dynamic correlation. The zeroth-order wavefunction generally needs to be of the multireference type, as exemplified in the FORS or CASSCF formalism, with an active space that includes all close lying electronic states. The dynamic correlation then must build on this zero-order wavefunction via multireference perturbation theory (e.g. MCQDPT) or singles and doubles multireference CI.

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- The most sophisticated methods for calculating SOC effects, combined with electronic structure methods that include an adequate treatment of dynamic correlation, are very computationally demanding with regard to both central processing unit time and computer resources. Therefore, in order to apply these methods to polyatomic molecules, the development of more efficient methodology will be essential. Such approaches will undoubtedly include new scalable software that takes advantage of massively parallel computers and more effective multireference methods. There is considerable current activity in both of these areas, so the prognosis is very encouraging.

Many of the methods to compute SOC in molecules described in this review are implemented in the publicly available and no-cost suite of quantum chemistry programs GAMESS (Schmidt *et al.* 1993).

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