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# An efficient treatment of kinematic factors in pseudo-relativistic calculations of electronic structure

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**Abstract.** Relativistic two-electron operators obtained by the Douglas-Kroll transformation contain p-dependent kinematic prefactors which are not present in the corresponding Breit-Pauli operators. These factors are usually calculated using a resolution of the identity approach, which requires integral transformations. In the present article we describe an alternative approach, based on a local approximation, where the effect of the prefactors can be absorbed in the atomic contraction coefficients. The effect of the local approximation is investigated in detail. The suggested approach is simple to implement in integral codes that allow the use of a general contraction scheme.

**Key words:** Relativistic effects – Contraction scheme – Spin-orbit coupling

## 1 Introduction

The study of transition-element chemistry and especially its role in catalytic processes is one of the most active areas in modern chemistry [1]. Understanding this chemistry has posed a challenge to theoretical chemists for a long time. The development of fast computers, effective algorithms and commonly available computer codes have made calculations on ground-state properties of molecules containing elements lighter than the second transition row almost a matter of routine.

For heavier elements relativistic effects become important for properties such as barriers, geometries and vibrational frequencies. First-order perturbation theory, which is available in most computer codes, gives accurate results for spin-free properties in the second-row transition elements, and relativistic effective core potentials have proven to be quite reliable also for the third transition row.

The Dirac and Breit equations provide the fundament for relativistic quantum chemistry [2]. The Dirac equation describes the movement of electrons in an external field, and contains both kinematic effects such as the mass increase with velocity and the effects of the interaction between the electron spin and the electromagnetic field. However, the solutions of the Dirac (and the Breit) equation are four-component spinors, and the method is rather complicated to use. Although the four-component methods have matured lately, and can now be applied to small and medium size molecules [3], they are still relatively resource-demanding and for larger systems more effective methods are needed. An alternative is provided by the Foldy-Wouthuysen transformation [4], which brings the original Dirac equation to an approximate two-component form. By adding perturbative corrections to the two-electron Coulomb operator we obtain the Breit-Pauli (BP) equations. These equations can be further simplified to the usual one-component form, familiar from non-relativistic theory, by neglecting the spin terms. Unfortunately the resulting equations are highly singular and can only be used in first-order perturbation calculations [5], where they often perform very well, however. An alternative is provided by the Douglas-Kroll (DK) transformation [6], which starts from the field-free Foldy-Wouthuysen (four-component) equation rather than the original Dirac equation. The DK method will be further addressed in Sect. 3 below.

Although complicated to use for molecules, the Dirac equation has been used in atomic calculations since Desclaux's work in the early 1970s [7]. Atomic calculations can also be done with the Cowan-Griffin method [8], which is essentially based on the Foldy-Wouthuysen transformation but the equations are stabilized by choosing appropriate boundary conditions. Accurate relativistic atomic calculations are necessary prerequisites for relativistic effective core potentials (RECPs), where relativity is included by fitting the effective core potential (ECP) parameters to relativistic atomic wave functions.

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In order to calculate, for example, the fine structure of atomic or molecular terms or the interaction between different spin states we need to include spin-orbit operators in the Hamiltonian.

The BP equation has been used with considerable success for the fine structure of the lighter elements. However, the BP spin-orbit operator is highly singular due to the $r^{-3}$ dependence, and for heavier elements the accuracy may deteriorate; for instance the error induced by the singular behaviour of the operator in the core region is of the order of $2000\,\mathrm{cm}^{-1}$ in the thallium atom [9, 10]. The effect of the DK transformation is to introduce kinematic factors which dampen the singularities in the original BP equation. Although the form of the operator does not change appreciably, the appearance of the kinematic factors has hitherto required a "resolution of identity" (RI) procedure in the integral calculation which has made the two-electron spin-orbit term very cumbersome.

The occurrence of the kinematic factors destroys some useful symmetry properties present in the original BP equation, and requires separate handling of each primitive integral. In the present work we suggest an efficient simplification, based on a local approximation, where the effect of the kinematic factors is absorbed in the atomic contraction coefficients. The computational effort is thus reduced to that of an ordinary BP calculation. The effect of the local approximation has been investigated by careful analysis of the two-electron part of the spin-orbit operator.

## 2 Basic theory

For cases where the total relativistic effects are small, they can be treated at the spin-free level as a perturbation on a non-relativistic system, and in an essentially non-relativistic formalistic framework. These pseudo-relativistic methods have been used for 20 years with considerable success.

The first major steps towards a computationally useful pseudo-relativistic variational approach were taken by Sucher [11], who developed the approach usually known as the "no-pair" (NP) method. The method attempts to eliminate positronic states through a unitary transformation derived from the Dirac equation for an electron in the absence of external fields. The name is related to the quantum electro-dynamic approach used in the original derivation and the justification of the approach (it is a little surprising that this works at all, since the effects of interest here are precisely those caused by the presence of a strong external field!). As the coupling between electronic and positronic states is eliminated the latter can be removed from further consideration. The equations involved are thus reduced in complexity, from the original four-component problem to one including only two components. (In the non-relativistic limit these two components correspond to the $\alpha$- and $\beta$-spin of a single, free electron, while in relativistic theory these states are no longer pure and well separated).

The Hamiltonian that results from the simple NP treatment has a structure not much different from the usual, non-relativistic Hamiltonian:

$$\hat{H}_+ = \sum_i (E_i + V_{\mathrm{eff}}(i)) + \sum_{i<j} V_{\mathrm{eff}}(i,j) \tag{1}$$

where

$$V_{\mathrm{eff}}(i) = A_i[V_{\mathrm{ext}}(i) + Q_i V_{\mathrm{ext}}(i) Q_i]A_i \ , \tag{2}$$

$$\begin{aligned} V_{\mathrm{eff}}(i,j) = A_i A_j \Bigg[ & \frac{1}{r_{ij}} + Q_i \frac{1}{r_{ij}} Q_i Q_j \frac{1}{r_{ij}} Q_j \\ & + Q_i Q_j \frac{1}{r_{ij}} Q_i Q_j \Bigg] A_i A_j + A_i A_j \big[ U_{ij} Q_i Q_j \\ & + Q_i U_{ij} Q_i + Q_j U_{ij} Q_i + Q_i Q_j U_{ij} \big] A_i A_j \ , \end{aligned} \tag{3}$$

$V_{\mathrm{ext}}(i) = -\sum_\mu \frac{Z_\mu}{|\mathbf{r}_i - \mathbf{r}_\mu|}$ is the usual, non-relativistic one-electron potential, $U_{ij}$ is the Breit term and

$$\begin{aligned} E_i &= (m^2c^4 + p_i^2c^2)^{1/2}; \\ A_i &= \left[\frac{E_i + mc^2}{2E_i}\right]; \\ Q_i &= c\frac{\sigma_i \mathbf{p}_i}{E_i + mc^2} \ , \end{aligned} \tag{4}$$

$\sigma_x, \sigma_y, \sigma_z$ are the usual Pauli spin matrices.

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

Using the Dirac relation $(\sigma\mathbf{u})(\sigma\mathbf{v}) = \mathbf{uv} + i\sigma(\mathbf{u}\times\mathbf{v})$ to separate spin and space coordinates, the complete NP operator is finally obtained:

$$\begin{aligned} H_{\mathrm{eff}}^{NP} = & \sum_i \Big( E_i + V_{\mathrm{eff}}^{sf}(i) + H^{SO}(i) \Big) \\ & + \sum_{i\neq j} \Big( V_{\mathrm{eff}}^{sf}(i,j) + H^{SO}(i,j) \Big) \ , \end{aligned} \tag{5}$$

$$V_{\mathrm{eff}}^{sf}(i) = A_i[V_{\mathrm{ext}}(i) + \mathbf{R}_i V_{\mathrm{ext}}(i) \mathbf{R}_i]A_i \ , \tag{6}$$

$$H^{SO}(i) = B_i \sum_{mu} \frac{Z_\mu}{|\mathbf{r}_i - \mathbf{r}_\mu|} (\mathbf{r}_i x \mathbf{p}_i) \sigma_i B_i \ , \tag{7}$$

$$\begin{aligned} V_{\mathrm{eff}}^{sf}(i,j) = A_i A_j \Bigg[ & \frac{1}{r_{ij}} + \mathbf{R}_i \frac{1}{r_{ij}} \mathbf{R}_i + \mathbf{R}_j \frac{1}{r_{ij}} \mathbf{R}_j \\ & + \mathbf{R}_i \left( \mathbf{R}_j \frac{1}{r_{ij}} \mathbf{R}_j \right) \mathbf{R}_i \Bigg] A_i A_j \ , \end{aligned} \tag{8}$$

$$H^{SO}(i,j) = -B_i A_j \hat{\mathbf{L}}_{ij} \sigma_i B_i A_j - 2A_i B_j \hat{\mathbf{L}}_{ij} \sigma_i B_i A_j \ , \tag{9}$$

$$\hat{\mathbf{L}}_{ij} = \frac{1}{r_{ij}^3}(r_{ij} \times \mathbf{p}_i) \ , \tag{10}$$

$$\mathbf{R}_i = \frac{c\mathbf{p}_i}{E_i + mc^2}; \quad B_i = \frac{A_i}{E_i + mc^2} \ . \tag{11}$$

The spin-spin and other small contributions have been neglected. In a refinement of the NP approach, Douglas and Kroll [6] attempted to reach a higher degree of de-coupling between the small and large component. Normally, the DK procedure is carried out only through the second order, and then only for the one-electron part of the Hamiltonian. The resulting, extra term in the effective Hamiltonian becomes:

$$H^{DK}_{\text{eff}} = H^{NP}_{\text{eff}} - \sum_i \tfrac{1}{2}\{\{E_i; W_1(i)\}; W_1(i)\} \ , \tag{12}$$

where the brackets { } denote an anti-commutator, $W_1$ is an integral operator with kernel

$$W_1(p_i; p_i') = A_i[Q_i - Q_i']A_i' \frac{V_{\text{ext}}(p_i, p_i')}{E_i - E_i'} \ , \tag{13}$$

where $V_{\text{ext}} * (p_i, p_i')$ is derived from the Fourier transform of the external potential. The computational implementation of the DK method by Hess et al. (see Ref. [12]) has gained a lot of attention and has been applied with success to a large number of chemical problems (see Ref. [13] and references therein). In cases where spin is not a major issue (in closed-shell systems and not extremely heavy elements) one can often neglect the latter and work in a spin-free formalism. The structure of this spin-free, one-component Hamiltonian is thus the same as in non-relativistic theory, and this structural "isomorphism" can be used to take advantage of the vast experience and code development for non-relativistic calculations. One-component, "pseudo-relativistic" calculations may be done on an almost routine basis, especially if the two-electron part of the Hamiltonian is treated totally non-relativistically, which is a commonly used approach. The inclusion of spin-orbit interaction is far more complicated and relatively few program systems including these terms are available.

The NP and DK methods can be contrasted to the BP approach, which is essentially a perturbation expansion where the zeroth-order Hamiltonian is furnished by the non-relativistic case, and the effect of relativity is treated perturbatively through the first order in $c^{-2}$. The BP approach has many similarities with DK theory, and the BP Hamiltonian can indeed be obtained from NP, through series expansion and truncation. For the spin-free parts of H one must go through a series expansion of $A$ and $B$, giving rise to a multitude of additional terms in the BP Hamiltonian, H. In contrast, the spin-orbit terms $H_{so}(i)$ are already of the order $c^{-2}$, and the corresponding $A = 1$, $B = 1/2c$. The DK and BP Hamiltonians thus have a very similar appearance, however, in actual applications they behave quite differently. The DK method has been found to provide a variationally stable effective Hamiltonian, and can thus be used in variational calculations. This is an important advantage over BP Hamiltonians which can only be used in perturbation calculations. One reason for this difference stems from the form of the spin-orbit operator which is highly singular due to the $r^{-3}$ term. The kinematic factors $A$ and $B$ in DK theory regularize the singularity to no worse than $r^{-1}$, which does not cause numerical problems.

## 3 Integrals in DK theory

While the kinematic factors have a stabilizing effect on the behaviour of the various operators in DK theory, they make the numerical procedure more complicated. Using the linear combination of atomic orbitals (LCAO) approximation in ab initio electronic structure theory, one must evaluate large numbers of one- and two-electron integrals of the basis functions over the various operators. The basis sets normally used in modern electronic structure theory are contracted Gaussians, i.e. functions of the form

$$\chi_t(r) = \sum_j c_{tj}\xi_j(r) \ , \tag{14}$$

where the primitive functions are given by

$$\xi_j(r) = x^{Lj}y^{Mj}z^{Nj}\exp\left[-\alpha_j r^2\right] \ . \tag{15}$$

With those basis functions, all the integrals which arise in the BP Hamiltonian can be obtained analytically. This is not the case in the DK formalism. The kinematic factors $A$, $B$ and $R$ are functions of the momentum [Eqs. (4) and (11)] bracketing other operators which are functions in coordinate space. This make the treatment of the Hamiltonians somewhat complicated, and numerical or other specialized techniques must be used. One approach often used in these contexts is the spectral resolution of the identity operator, i.e. $\hat{I} = (\sum |k\rangle\langle k|)$ where the sum encompasses a complete set of orthonormal functions $|k\rangle$.

For the matrix representation of a product of operators $AB$, one then obtains:

$$\begin{aligned}[\hat{A}\hat{B}]_{ij} &= \langle i|\hat{A}\hat{B}|j\rangle = \sum_k \langle i|\hat{A}|k\rangle\langle k|\hat{B}|j\rangle \\ &= \sum_k [\hat{A}]_{ik}[\hat{B}]_{kj} = (\mathbf{AB})_{ij} \ .\end{aligned} \tag{16}$$

We have used square brackets [ ] to denote a matrix representation of an operator, and bold-face symbols for matrices, i.e. $\mathbf{A} \equiv [\hat{A}], \mathbf{B} \equiv [\hat{B}]$. Equation (16) simply states that the matrix representation of a product of operators is the product of the matrix representations in a complete, orthonormal basis. In a non-orthogonal representation with metric S, the expression becomes

$$[\hat{A}\hat{B}]_{ij} = (\mathbf{AS}^{-1}\mathbf{B})_{ij} \tag{17}$$

and with an incomplete basis, Eqs. (16) and (17) are only approximate. A generalization of this theorem states that the matrix representation of a function of an operator equals the function of the matrix representation (still assuming a complete, orthonormal basis):

$$[f(\hat{A})]_{ij} = (f(\mathbf{A}))_{ij} \ . \tag{18}$$

It is easy to see how these ideas can be used to evaluate matrix elements of the algebraically complicated operators that arise in the DK formalism. The operators can all be written as products of the simpler BP operators, and various prefactors. The latter are all functions of $p^2$ and their matrix representation can therefore be obtained through Eq. (17). Once all these matrices are evaluated, Eq. (18) can be applied to obtain a matrix representation of the different terms in the DK Hamiltonian. The one-electron operators are generally of the form

$$\hat{Q}^{DK} = \hat{C}\hat{Q}\hat{D} \tag{19}$$

where $\hat{Q}$ is the operator in BP theory, and $\hat{C}$ and $\hat{D}$ are the extra prefactors that arise in DK theory. The integrals to be evaluated over two basis functions $\chi_t$ and $\chi_u$ are of the form

$$\left\langle \chi_t \middle| \hat{Q}^{DK} \middle| \chi_u \right\rangle \ , \tag{20}$$

which can be written with the above techniques as

$$\left\langle \chi_t \middle| \hat{C}\hat{Q}\hat{D} \middle| \chi_u \right\rangle = (\mathrm{CS}^{-1}\mathbf{QS}^{-1}\mathbf{D})_{tu} \ . \tag{21}$$

The approach outlined above is heavily based on a spectral resolution of the identity operator, and is often referred to as the RI approach. It is also possible to use modifications of these techniques and approximations to deal with the prefactors in DK theory.

$$\left\langle \chi_t \middle| \hat{Q}^{DK} \middle| \chi_u \right\rangle = \left\langle \chi_t \middle| \hat{C}\hat{Q}\hat{D} \middle| \chi_u \right\rangle = \left\langle \hat{C}\chi_t \middle| \hat{Q} \middle| \hat{D}\chi_u \right\rangle \ . \tag{22}$$

One can approach this problem from the point of view of re-expanding the functions $\phi_t(\mathbf{r}) = \hat{C}\chi_t(\mathbf{r})$ and $\phi_u(\mathbf{r}) = \hat{D}\chi_u(\mathbf{r})$ in the original basis set, e.g.:

$$\phi_t(\mathbf{r}) = \hat{C}\chi_t(\mathbf{r}) = \sum_i c'_{ti}\chi_i(\mathbf{r}) \tag{23}$$

where $\chi_i(\mathbf{r})$ are usual, contracted Gaussian basis functions. To define the expansion coefficients $c'_{ti}$, some criterion on the "best" fit must be applied. One can for instance require the residual function $R_t(\mathbf{r}) = \hat{C}$ $\chi_t(\mathbf{r}) - \sum_i c'_{ij}\chi_i(\mathbf{r})$ to be minimized in a least-squares sense, i.e. that the coefficients minimize the integral $\int |R_t(\mathbf{r})|^2 d^3\mathbf{r}$. This gives an expression $\mathrm{c} = \mathrm{S}^{-1}\mathrm{C}^{+}$ the expansion coefficients, which leads to identically the same result as with the RI approach. It is worth noting, however, that other criteria for a "best" re-expansion Eq. (23) would give different integral expressions, and thus slightly different numerical values for the resulting integrals.

## 4 The one-centre expansion approximation

While both the RI and the expansion method allow for an evaluation of the necessary integrals in DK theory to a fairly good approximation, some practical problems remain. The application of the prefactor transformation for the two-electron operators amounts to full four-index transformations of all the two-electron integrals, both for the spin-orbit interaction and in the spin-free case. In addition to the use of a basis set for the LCAO expansion of orbitals, the basis set is used to express the effective Hamiltonian itself. As a consequence, the Hamiltonian depends on the basis set and thus on the geometry, not only through the nuclear coordinates, as one would expect, but also artificially through the RI or the re-expansion technique. This leads to problems of basis set superposition (BSSE) which are difficult to control, since no variational principle governs the errors caused by this basis set effect on the Hamiltonian. An alternative, simplified approach will therefore be described.

It can easily be shown that the result of the operator $p^2 = -\hbar^2\nabla^2$ acting on a Gaussian basis function is simply another sum of Gaussians, all centred on the same atom. The same is true for any power of $p^2$, and therefore also for the prefactors $A$ and $B$, which are functions of $p^2$. One may therefore conclude that the function $\phi_t(\mathbf{r})$ in Eq. (23) is a modified function centred on the same atom as $\chi_t(\mathbf{r})$. We therefore try to expand $\phi_t(\mathbf{r})$ in the same primitive basis set as $\phi_t(\mathbf{r})$ in Eq. (23), i.e.

$$\phi_t(\mathbf{r}) = \hat{B}\chi_t(\mathbf{r}) = \sum_j c'_{tj}\xi_j(\mathbf{r}) \ . \tag{24}$$

When a basis function $\chi_t(\mathbf{r})$ is diffuse, the prefactor B will have little effect on it, and the expansion coefficients $c'_{tj}$ will be nearly the same as the original contraction coefficients (apart from a factor).

This approach would allow the effect of the prefactors to be incorporated into an ordinary integral code for BP integrals, simply through modification of the contraction coefficients used in the original code. Of course, one can treat the spin-free operators in the same spirit, accounting for the prefactors through the use of modified contraction coefficients.

This approach has several advantages. The application of prefactors to the two-electron operators is greatly simplified, no additional BSSE problems are introduced since the projection basis set used internally is totally geometry independent, and gradient evaluation is not more complicated than in the non-relativistic case.

## 5 The two-electron spin-orbit integrals

In the two-electron spin-orbit interaction term Hso(i,j) we distinguish two terms: the spin-same-orbit (SSO) part and the spin-other-orbit (SOO) interaction, where the former term describes the interaction of an electron's spin with its own angular moment due to the field from another electron and the latter the interaction of the spin of one electron with the magnetic moment of another. The physical interpretation of these terms is quite different, even though they happen to have similar physical appearance. This similarity is even more pronounced in the BP formalism, where the operator has the form:

$$H^{SO}_{BP}(i,j) = -\hat{\mathbf{L}}_{ij} \cdot (\sigma_i + 2\sigma_j) \ . \tag{25}$$

The integrals involving the spin-orbit operator are given by

$$\left\langle ac \middle| \hat{\mathbf{L}}_{12} \cdot \sigma_1 \middle| bd \right\rangle = \mathbf{L}_{abcd} \cdot \sigma_{abcd} \ , \tag{26}$$

where we have introduced the notation $\mathbf{L}_{abcd}$ for the spatial integral $\langle ac|\hat{\mathbf{L}}|bd\rangle$, and where spin-integration gives $\sigma_{abcd} = (a\sigma b)\cdot(cd)_s$. Upon permutation of the orbital indices, we obtain:

$$\mathbf{L}_{abcd} = -\mathbf{L}^{*}_{badc}$$

$(= \mathbf{L}_{abdc} = -\mathbf{L}_{bacd}$ if the orbitals are real), and also

$$\langle ac|\hat{\mathbf{L}}_{21}|bd\rangle = -\langle ca|\hat{\mathbf{L}}_{21}db\rangle = -\mathbf{L}cdab \ . \tag{28}$$

But since the interaction is asymmetric in the two electrons involved there is no relation between $L_{cdab}$ and $L_{abcd}$, in contrast to the usual two-electron integrals over the Coulomb repulsion operator. For the DK Hamiltonian, the expression takes a less symmetric form than in BP theory due to the occurrence of the prefactors $A$ and $B$. With the use of the RI techniques discussed in the previous section, we obtain

$$\begin{aligned}\hat{H}^{DK}_{SO} = &- \sigma_{pqrs}(B_{ap}B_{bq}\mathbf{L}_{pqrs}\sigma_{abcd}A_{cr}A_{ds} \\ &+ 2A_{ap}B_{bq}\mathbf{L}_{pqrs}\sigma_{abcd}B_{cr}A_{ds}) \ .\end{aligned} \tag{29}$$

For the integrals involved, we note that $B_{ap}B_{bq}\mathbf{L}_{pqrs}A_{cr}A_{ds}$ has the same permutational symmetry as $\mathbf{L}_{abcd}$, whereas $A_{ap}B_{bq}\mathbf{L}_{pqrs}B_{cr}A_{ds}$ possesses no permutational symmetry at all.

We define the following two operators

$$\hat{\mathbf{X}}_{ij} = B_iA_j\hat{\mathbf{L}}_{ij}B_iA_j \ , \tag{30}$$

$$\hat{\mathbf{Y}}_{ij} = B_jA_i\hat{\mathbf{L}}_{ij}B_iA_j \ , \tag{31}$$

which make the DK operator take the following form

$$\hat{H}^{DK}_{SO} = \sum_{ij}\left(\hat{\mathbf{X}}_{ij}\mathbf{s}_i + 2\hat{\mathbf{Y}}_{ij}\mathbf{s}_j\right) = \sum_{ij}\left(\hat{\mathbf{X}}_{ij} + 2\hat{\mathbf{Y}}_{ij}\right)\right) \cdot \mathbf{s}_i \ . \tag{32}$$

Defining

$$\hat{\mathbf{Z}}_{ij} = \frac{-\mathbf{X}_{ij} + 2\mathbf{X}_{ji} - 2\mathbf{Y}_{ji} + 4\mathbf{Y}_{ij}}{3} \tag{33}$$

one finds that

$$\mathbf{Z}_{ij} + 2\mathbf{Z}_{ji} = \mathbf{X}_{ij} + 2\mathbf{Y}_{ji} \ . \tag{34}$$

$\hat{\mathbf{L}}$ is the original BP formalism can then be replaced by $\hat{\mathbf{Z}}$.

Introducing $\underline{\underline{x}} = Bx$ and $\underline{x} = Ax$ we can write:

$$\begin{aligned}\mathbf{X}_{abcd} &= \langle acB_1A_2|\hat{\mathbf{L}}_{12}|B_1A_2bd\rangle \\ &= \left\langle \underline{\underline{a}}\underline{c}|\hat{\mathbf{L}}_{12}|\underline{\underline{b}}\underline{d}\right\rangle \\ &= (\underline{\underline{a}}\underline{\underline{b}}|\underline{c}\underline{d}) = [ab|cd] \ ,\end{aligned} \tag{35}$$

and $\hat{\mathbf{X}}$ has the same symmetry as $\hat{\mathbf{L}}$.

For $\hat{\mathbf{Y}}$, however, we have

$$\mathbf{Y}_{abcd} = \langle acB_2A_1\hat{\mathbf{L}}_{12}|B_1A_2bd\rangle = \left\langle \underline{a}\underline{\underline{c}}\middle|\hat{\mathbf{L}}_{12}\underline{\underline{b}}\underline{d}\right\rangle = (\underline{a}\underline{\underline{b}}|\underline{\underline{c}}\underline{d}) \tag{36}$$

but

$$\mathbf{Y}_{abdc} = (\underline{a}\underline{\underline{b}}|\underline{\underline{d}}\underline{c}) = (\underline{a}\underline{\underline{b}}|\underline{c}\underline{\underline{d}}) \neq (\underline{a}\underline{\underline{b}}|\underline{\underline{c}}\underline{d})$$

$$\mathbf{Y}_{bacd} = (\underline{b}\underline{\underline{a}}|\underline{\underline{c}}\underline{d}) = (\underline{\underline{a}}\underline{b}|\underline{\underline{c}}\underline{d}) \neq (\underline{a}\underline{\underline{b}}|\underline{\underline{c}}\underline{d})$$

$$\mathbf{Y}_{badc} = -(\underline{b}\underline{\underline{a}}|\underline{\underline{c}}\underline{d}) = (\underline{\underline{a}}\underline{b}|\underline{c}\underline{\underline{d}}) \neq (\underline{a}\underline{\underline{b}}|\underline{\underline{c}}\underline{d}) \ . \tag{37}$$

In a computer code based on BP formalism, these four integrals will be treated identically. Thus, it is desirable to form the appropriate average in the integral program:

$$\{ab|cd\} = \tfrac{1}{4}[(\underline{a}\underline{\underline{b}}|\underline{\underline{c}}\underline{d}) + (\underline{a}\underline{\underline{b}}|\underline{c}\underline{\underline{d}}) + (\underline{\underline{a}}\underline{b}|\underline{\underline{c}}\underline{d}) + (\underline{\underline{a}}\underline{b}|\underline{c}\underline{\underline{d}})] \ . \tag{38}$$

For the SOO terms, we get:

$$\begin{aligned}\hat{\mathbf{Y}}_{21,abcd} &= \langle acB_1A_2\hat{\mathbf{L}}_{21}|B_2A_1bd\rangle \\ &= \left\langle \underline{\underline{a}}\underline{c}\hat{\mathbf{L}}_{21}\underline{b}\underline{\underline{d}}\right\rangle \\ &= -\left\langle \underline{c}\underline{\underline{a}}|\hat{\mathbf{L}}_{12}\underline{\underline{d}}\underline{b}\right\rangle \\ &= -(\underline{c}\underline{\underline{d}}|\underline{\underline{a}}\underline{b})\end{aligned} \tag{39}$$

which also should be averaged in the integral code.

Finally,

$$\begin{aligned}(ab|\mathbf{Z}_{\mathrm{ij}}|cd) = \tfrac{1}{3}(&-[ab|cd] + 2[cd|ab] - 2\{cd|ab\} \\ &+ 4\{ab|cd\}) \ .\end{aligned}$$

## 6 Practical computational considerations

While the technique with contraction coefficients described above is a feasible way to incorporate the kinematic prefactors, it is still a fairly complicated procedure. Two different sets of modified coefficients are needed (one for each prefactors $A$ and $B$) and the SOO term needs to be contracted in four different ways in order to maintain the BP structure of the program. Alternatively, a file of two-electron integrals completely without symmetry needs to be created.

There is ample evidence that the two-electron spin-orbit term is dominated by the SSO part [14]. The SOO interaction is typically more than an order of magnitude smaller than the SSO term, and falls in the same category as other small two-electron effects, such as spin-spin and orbit-orbit interactions. The SOO term can thus be omitted in most calculations without any serious loss of accuracy. This will allow the use of existing integral programs almost without modifications. There is no principle difficulty in implementing the method of contraction coefficients including the SOO term, it just takes more effort in handling the integrals in the sorting step. This has in fact already been done in the mean-field [15] spin-orbit integral program AMFI [16]. Finally, the statement of the local character of the prefactors should be tested. We have done this for the one-electron spin-orbit term through calculations on several states of $Br_2$ and $I_2$ using the total primitive basis in the RI procedure and by using the suggested methods of contraction coefficients.

## 7 Computational details

### 7.1 Basis sets

The bromine basis set consists of (16*s* 13*p* 8*d*) primitive Gaussian type orbitals [17] contracted to [6*s* 5*p* 2*d*] using a general Rafenetti contraction [18]. For iodine an uncontracted (20*s* 16*p* 11*d*) atomic basis set [19] was contracted to [7*s* 6*p* 3*d*]. The contraction coefficients were for both Br and I determined from atomic relativistic NP calculations on $^2P$ ground state. Both the bromine and iodine basis sets were extended with correlating *d*- and *f*-functions, with the exponents 0.24 and 0.54 for bromine and 0.22 and 0.39 for iodine [20].

### *7.2 Calculations*

All the calculations were carried out in the $D_{2h}$ group symmetry. Integrals were generated by a version of the program HERMIT [21] extended to include scalar and spin-orbit integrals over the second-order DK operator. This modified version of the program contains the possibility to calculate the one-electron spin-orbit integrals both by the usual full RI approach and by a one-centre expansion. The Hartree-Fock (HF) calculations on the $\Lambda$ reference state were performed with the program SIRIUS [22]. The orbitals from HF calculations on the $O_g^+$ ($^1\Sigma_g^+$) state were used as reference orbitals in the following configuration interaction (CI) calculations. The internuclear distance was set to 4.42 and 5.18 a.u. for $Br_2$ and $I_2$, respectively. The spin-orbit CI calculations were carried out using only the one-electron spin-robit operator in an internal CI space defined by redistributing four electrons in the $\pi_g$ and the $\sigma_u$ molecular orbitals. The former is fully occupied and the latter empty in the molecular ground state.

This is certainly a very small active space and the $\sigma_u$ orbital determined from a ground-state calculation will be far from optimal for the excited states and, moreover, we only used the one-electron part of the spin-orbit operator. However, the aim of the present study is to demonstrate the accuracy of the one-centre expansion method, not to reproduce experimental results, and for that purpose the quality of the calculations is satisfactory.

## 8 Results

Results obtained for $Br_2$ and for $I_2$ are shown in Tables 1 and 2, respectively. The selection rules for the spin-orbit operator is $\Lambda \rightarrow \Lambda \pm 1$ and $\sigma \rightarrow \sigma \pm 1$. In our small spin-orbit calculation the only significant interactions occur between the $^3\Sigma_g^-$ and the $^1\Sigma_g^+$ states, and the $^3\Pi_u$ and the $^1\Pi_u$ states. It should again be emphasized that the calculations are very constrained, and a larger calculation might change this result.

However, the main point with the calculations was to investigate the accuracy of the one-centre expansion method. By comparing the numbers in the last two columns in Tables 1 and 2, we see that essentially no accuracy is lost. The differences are at most in the order of a few thousandth of a wave number, or $10^{-8}$ atomic units, and we may safely conclude that the one-centre approximation can be used with confidence. This result

**Table 1.** Results obtained for $Br_2$ using the resolution of the identity (RI) approach and the one-center expansion method. All energies in $cm^{-1}$

| Non-relativistic state | Energy | Relativistic state | RI | 1 approx. |
|---|---|---|---|---|
| $^1\Sigma^+$ | 0.00 | $^1\Sigma_0^+$ | 0.00 | 0.00 |
| $^3\Pi u$ | 14251.21 | $^3\Pi_2$ | 12909.2279 | 12909.2299 |
| | | $0.04\,^1\Pi_1 + 0.96\,^3\Pi_1$ | 13989.8675 | 13989.8683 |
| | | $^3\Pi_0$ | 15613.3990 | 15613.3969 |
| $^1\Pi u$ | 20723.42 | $0.96\,^1\Pi_1 + 0.04\,^3\Pi_1$ | 20996.1182 | 20996.1174 |
| $^3\Sigma^-$ | 29683.11 | $0.83\,^1\Sigma_0^- + 0.17\,^3\Sigma_0^+$ | 28525.4619 | 28525.4649 |
| | | $^3\Sigma_1^-$ | 29684.3616 | 29684.3616 |
| $^1\Delta$ | 32136.36 | $^1\Delta_2$ | 32137.6138 | 32137.6714 |
| $^1\Sigma+$ | 34311.83 | $0.17\,^1\Sigma_0^- + 0.83\,^3\Sigma_0^+$ | 35469.9405 | 35469.9376 |

**Table 2.** Results obtained for $I_2$ using the RI approach and the one-center expansion method. All energies in $cm^{-1}$

| Non-relativistic state | Two-center ($cm^{-1}$) | Relativistic state | Two-center ($cm^{-1}$) | One-center ($cm^{-1}$) |
|---|---|---|---|---|
| $^1\Sigma^+$ | 0.00 | $^1\Sigma_0^+$ | 0.00 | 0.00 |
| $^3\Pi u$ | 12205.76 | $^3\Pi_2$ | 9512.8100 | 9512.8097 |
| | | $0.13\,^1\Pi_1 + 0.87\,^3\Pi_1$ | 11152.7063 | 11152.7061 |
| | | $^3\Pi_0$ | 14909.7953 | 14909.7957 |
| $^1\Pi u$ | 18026.06 | $0.87\,^1\Pi_1 + 0.13\,^3\Pi_1$ | 19090.0930 | 19090.0933 |
| $^3\Sigma^-$ | 24933.36 | $0.67\,^1\Sigma_0^- + 0.33\,^3\Sigma_0^+$ | 21313.8926 | 21313.8920 |
| | | $^3\Sigma_1^-$ | 24938.8057 | 24938.8057 |
| $^1\Delta$ | 26911.24 | $^1\Delta_2$ | 26916.6665 | 26916.6665 |
| $^1\Sigma+$ | 28650.67 | $0.33\,^1\Sigma_0^- + 0.67\,^3\Sigma_0^+$ | 32286.4890 | 32286.4896 |

is very encouraging, since the computational gain achieved by this approximation is very large.

## 9 Conclusions

In the present paper we have discussed the problems arising from the kinematic prefactors occurring in the DK operators. Based on the assumption that the DK two-electron operators are local, we suggest a scheme where the effect of the kinematic factors is absorbed in the atomic contraction coefficients. Since the effect of the kinematic factors is described by modified atomic contraction coefficients the method is simple to implement in integral codes that allow the use of a general contraction scheme. Test calculations on $Br_2$ and $I_2$ showed that the one-centre approximation results in virtually no loss of accuracy.

Previous calculations on the T1 atom have shown that it is very important to include the kinematic factors in the Hamiltonian [9, 10]. The method suggested in this paper makes it possible to include the kinematic factors at a low computational cost. In particular, if the SOO term is neglected existing program packages for molecular one- and two-centre spin-orbit integrals can be used almost without any changes.

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## References

1. Sauer J (1989) Chem Rev In: Lipkowittz KB, Boyd DB (eds) 89:199
2. Almöf J, Gropen O (1996) Reviews in computational chemistry, vol 8. VCH, New York, pp 203
3. Visscher L, Saue T, Nieuport WC, Faegri K, Gropen O (1993) J Chem Phys 99:6704–6715
4. Foldy LL, Wouthuysen SA (1950) Phys Rev 78:29
5. Moss RE (1973) In: Advanced molecular quantum mechanics. Chapman and Hall, London
6. Douglas M, Kroll NM (1974) Ann Phys 82:89–155
7. Desclaux JP (1975) Comput Phys Commun 9:31
8. Cowan RO, Griffin DC (1976) J Opt Soc Am 66, 1010
9. Rakowitz F, Marian CM (1996) Chem Phys Lett 257:105
10. Wahlgren U, Sjövoll M, Fagerli H, Gropen O, Schimmelpfennig B (1997) Theor Chem Actc 97:324
11. Sucher J (1980) Phys Rev A 22:348
12. Hess BA (1986) Phys Rev A 33:3742
13. Pyykkö P (1988) Chem Rev 88:563–594
14. Saxena KMS, Malli G (1968) Can J Phys 48:1088; (1968) Can J Phys 47:2805; (1971) Int J Quantum Chem S5:619
15. Hess BA, Marian CM, Wahlgren U, Gropen O (1996) Chem Phys Lett 251:365
16. Schimmelpfennig B (1996) An Atomic Mean Field Integral (AMFI) program Stockholm
17. Faegri K (personal communication)
18. Rafenetti RC (1973) J Chem Phys 58:4452
19. Faegri K (personal communication)
20. Dyall K, Visscher L (1996) J Chem Phys 104:2040
21. HERMIT, a molecular integral program written by Helgaker T, Taylor PR, Ruud K, Vahtras O, Koch H, University of Oslo
22. SIRIUS a program for calculation of MCSCF wavefunctions written by Jensen HJ, Ågren H, Olsen J (1990) Motecc-g, Chapt. 8