The calculation of atomic and molecular spin-orbit coupling matrix elements

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I. INTRODUCTION

We write the electronic Hamiltonian as $\hat{H}_{el}(\vec{r},\vec{R})$, where $\vec{r}$ and $\vec{R}$ denote, collectively, the positions of the electrons and nuclei, respectively. This operator includes the kinetic energy of the electrons and all electron-nuclei and electron-electron Coulomb interactions, but neglects the much weaker interaction between the magnetic moments generated by the orbital motion and spin of the electrons. The spin-orbit Hamiltonian for an N-electron system can be written as

$$H_{so} = \sum_i \hat{a}_i \vec{l}_i \cdot \vec{s}_i = \sum_i \hat{a}_i \left(l_{x_i} s_{x_i} + l_{y_i} s_{y_i} + l_{z_i} s_{z_i}\right) = \sum_i \hat{a}_i \left[l_{z_i} s_{z_i} + \tfrac{1}{2}\left(l_{i+} s_{i-} + l_{i-} s_{i+}\right)\right]$$

Here $\hat{a}_i$ is a one-electron operator which depends on the radial part of the electronic wavefunction. [1]

In this Chapter we shall explore the determination of the matrix of the spin-orbit Hamiltonian for several atomic and molecular systems, and make reference to Molpro input files for the calculation of expectation value of $\hat{a}$.

II. ATOMS

A. p^1 electron occupancy

Consider an atom with a single electron in a p state. This can be the excited state of the H atom, the excited state of an alkali metal atom, or the ground state of the group IIIb elements (B, Al, ...). There are six possible states: the product of the three possible projection states of the orbital electronic angular momentum $m = 1, 0, -1$ and the two possible spin states $m_s = \pm 1/2$. We will abbreviate the wavefunctions for these states using a Slater determinantal notation as $|p_1|$, $|\bar{p}_1|$, ... $|\bar{p}_{-1}|$. In this six-state basis, the matrix of the spin-orbit Hamiltonian is

$$\mathbf{H}_{so}^{(m)} = \frac{a}{2} \left(\begin{array}{c|cccccc} & p_1 & \bar{p}_1 & p_0 & \bar{p}_0 & p_{-1} & \bar{p}_{-1} \\ \hline p_1 & 1 & 0 & 0 & 0 & 0 & 0 \\ \bar{p}_1 & 0 & -1 & \sqrt{2} & 0 & 0 & 0 \\ p_0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ \bar{p}_0 & 0 & 0 & 0 & 0 & \sqrt{2} & 0 \\ p_{-1} & 0 & 0 & 0 & \sqrt{2} & -1 & 0 \\ \bar{p}_{-1} & 0 & 0 & 0 & 0 & 0 & 1 \end{array} \right) \qquad (1)$$

Here, the superscript "(m)" denotes the definite-m representation. Diagonalization gives eigenvalues of $-a$ (two-fold degenerate) and $a/2$ (four-fold degenerate), as we would anticipate.

1. *Transformation from definite-m to Cartesian basis: Fundamentals*

Instead of definite-m states we can use the Cartesian p states, which we define as

$$p_x = 2^{-1/2}\left(-p_1 + p_{-1}\right), \tag{2}$$

$$p_y = 2^{-1/2} i \left(p_1 + p_{-1}\right), \tag{3}$$

and

$$p_z = p_0. \tag{4}$$

The definition of p_x and p_y are those given in Sec. 2.1 of Wikipedia's Table of Spherical Harmonics, and follows from the usual definition of the definite-m spherical harmonics, namely

$$p_1 = -2^{-1/2}\left(p_x + ip_y\right),$$

$$p_{-1} = 2^{-1/2}\left(p_x - ip_y\right).$$

Consider a general operator $\hat{A}$ (which for the purpose of demonstration we shall take here to be $\hat{A} = l_z s_z$). In the definite-m basis, we can use the closure relation

$$\mathbf{1} = \sum_m |m\rangle\langle m|$$

to express $\hat{A}$ in the definite-m basis as

$$\hat{A} = \sum_{m,m'} |m\rangle\langle m|\hat{A}|m'\rangle\langle m'| = \sum_{m,m'} |m\rangle\langle m|\hat{A}|m'\rangle\langle m'| = \sum_{m,m'} |m\rangle A_{mm'}\langle m'|$$

We this, we can write any matrix of $\hat{A}$ in the Cartesian basis as

$$A_{qq'} = \langle q|\hat{A}|q'\rangle = \sum_{mm'} \langle q|m\rangle A_{mm'} \langle m'|q'\rangle \tag{5}$$

For demonstration purposes, let us use just two definite-m states $|m = 1\rangle$ and $|m = -1\rangle$ and two Cartesian states $|x\rangle$ and $|y\rangle$. Then, we can use Eq. (5) to express the four matrix elements of the 2×2 matrix of $\hat{A}$ in the Cartesian basis as follows:

$$A_{xx} = \langle x|1\rangle A_{11}\langle 1|x\rangle + \langle x|-1\rangle A_{-1,-1}\langle -1|x\rangle + \langle x|1\rangle A_{1,-1}\langle -1|x\rangle + \langle x|-1\rangle A_{-1,1}\langle 1|x\rangle$$

$$A_{xy} = \langle x|1\rangle A_{11}\langle 1|y\rangle + \langle x|-1\rangle A_{-1,-1}\langle -1|y\rangle + \langle x|1\rangle A_{1,-1}\langle -1|y\rangle + \langle x|-1\rangle A_{-1,1}\langle 1|y\rangle$$

$$A_{yx} = \langle y|1\rangle A_{11}\langle 1|x\rangle + \langle y|-1\rangle A_{-1,-1}\langle -1|x\rangle + \langle y|1\rangle A_{1,-1}\langle -1|x\rangle + \langle y|-1\rangle A_{-1,1}\langle 1|x\rangle$$

$$A_{xy} = \langle y|1\rangle A_{11}\langle 1|y\rangle + \langle y|-1\rangle A_{-1,-1}\langle -1|y\rangle + \langle y|1\rangle A_{1,-1}\langle -1|y\rangle + \langle y|-1\rangle A_{-1,1}\langle 1|y\rangle$$

We can rewrite these four equations in matrix notation as

$$\begin{pmatrix} A_{xx} & A_{xy} \\ A_{yx} & A_{yy} \end{pmatrix} = \begin{pmatrix} \langle x|\,1\rangle & \langle x|\,-1\rangle \\ \langle y|\,1\rangle & \langle y|\,-1\rangle \end{pmatrix} \begin{pmatrix} A_{11} & A_{1-1} \\ A_{-11} & A_{-1-1} \end{pmatrix} \begin{pmatrix} \langle 1|\,x\rangle & \langle 1|\,y\rangle \\ \langle -1|\,x\rangle & \langle -1|\,y\rangle \end{pmatrix} \tag{6}$$

We now define a matrix T, which transforms from the definite-m to the Cartesian basis, as

$$T_{jk} \equiv \langle q_j|\,m_k\rangle \tag{7}$$

We also know that in general any matrix element and its transpose satisfy the equality

$$\langle j|k\rangle = \langle k|j\rangle^*$$

then Eq. (6) can be written as

$$\mathbf{A}^{(q)} = \mathbf{T}\,\mathbf{A}^{(m)}\mathbf{T}^\dagger \tag{8}$$

where the Hermitian adjoint of a matrix is the complex conjugate of the transpose, namely $\mathbf{T}^\dagger = (\mathbf{T}^T)^*$.

2. *Full (coupled) transformation to the Cartesian basis*

The transformation from the six definite-m p-spin orbitals to the six Cartesian p-spin orbitals is defined similarly to Eq. (7), namely

$$\mathbf{T} = 2^{-1/2} \begin{pmatrix} -1 & 0 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 0 & 1 \\ -i & 0 & 0 & 0 & -i & 0 \\ 0 & -i & 0 & 0 & 0 & -i \\ 0 & 0 & \sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2} & 0 & 0 \end{pmatrix} \tag{9}$$

This is a unitary transformation, so that $\mathbf{T}\mathbf{T}^\dagger = \mathbf{T}^\dagger\mathbf{T} = \mathbf{1}$.

Thus, in the basis of the six Cartesian spin-orbitals, the matrix of the spin-orbit Hamiltonian is

$$\mathbf{H}_{so}^{(q)}(p^1) = \mathbf{T}\,\mathbf{H}_{so}^{(m)}(p^1)\,\mathbf{T}^\dagger = \frac{a}{2} \left(\begin{array}{c|cccccc} & p_x & \bar{p}_x & p_y & \bar{p}_y & p_z & \bar{p}_z \\ \hline p_x & 0 & 0 & -i & 0 & 0 & 1 \\ \bar{p}_x & 0 & 0 & 0 & i & -1 & 0 \\ p_y & i & 0 & 0 & 0 & 0 & -i \\ \bar{p}_y & 0 & -i & 0 & 0 & -i & 0 \\ p_z & 0 & -1 & 0 & i & 0 & 0 \\ \bar{p}_z & 1 & 0 & i & 0 & 0 & 0 \end{array} \right) \tag{10}$$

This is identical to the matrix of the spin-operator that we would obtain from a Molpro calculation on the B atom, as would be done with the input file `b_so.com`

3. *Decoupled transformation to the Cartesian basis*

Alternatively, one can use the spin-orbit operator in the full Cartesian representation

$$H_{so} = \sum_i \hat{a}_i \vec{l} \cdot \vec{s} = \sum_i \hat{a}_i \left(l_x s_x + l_y s_y + l_z s_z \right) \tag{11}$$

and designate, explicity, the separate orbital and spin dependence of the individual states as, for example, $p_x \equiv |p_x\rangle\,|1/2\rangle$ or $\bar{p}_y \equiv |p_y\rangle\,|-1/2\rangle$. Then, to determine the matrix of the spin-orbit Hamiltonian, we need to determine, separately, the matrices of l_x, l_y, and l_z in the basis of the three spin-free Cartesian p_q states and the matrices of s_x, s_y, and s_z in the two $m_s = \pm 1/2$ states. The latter are the three Pauli matrices, namely

$$\mathbf{s}_x = \frac{1}{2}\left(\begin{array}{c|cc} & 1/2 & -1/2 \\ \hline 1/2 & 0 & 1 \\ -1/2 & 1 & 0 \end{array}\right)$$

and, suppressing the row and column labels,

$$\mathbf{s}_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

and

$$\mathbf{s}_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The equivalent Pauli matrices for the $l = 1$ states are (where we assume the states are ordered $m = 1$, $m = 0$, $m = -1$)

$$\mathbf{l}_x^{(m)} = 2^{-1/2}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\mathbf{l}_y^{(m)} = 2^{-1/2}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

and

$$\mathbf{l}_z^{(m)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Now, to convert the $l = 1$ Pauli matrices into the spin-free Cartesian basis we use the spin-free equivalent to Eq. (17), namely

$$\mathbf{T} = 2^{-1/2} \begin{pmatrix} -1 & 0 & 1 \\ -i & 0 & -i \\ 0 & \sqrt{2} & 0 \end{pmatrix}$$

which gives

$$\mathbf{l}_x^{(q)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

$$\mathbf{l}_y^{(q)} = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}$$

and

$$\mathbf{l}_z^{(q)} = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Using these matrix representations of $\mathbf{l}_{x,y,z}$ and $\mathbf{s}_{x,y,z}$ and the Cartesian expression for the spin-orbit operator [Eq. (11)] we can obtain an equation for the matrix of $\hat{H}_{so}$ in the six-state Cartesian representation that is identical to Eq. (10). The advantage of using this decoupled Cartesian representation is that we can identify which of the three spin-orbit operators $l_x s_x$, $l_y s_y$ or $l_z s_z$ contributes to each matrix element in the 6 *times*6 matrix in Eq. (10). To indicate this, we annotate the matrix here in red.

$$\mathbf{H}_{so}^{(q)}(p^1) = \mathbf{T}\,\mathbf{H}_{so}^{(m)}(p^1)\,\mathbf{T}^\dagger = \frac{a}{2} \left(\begin{array}{c|cccccc} & p_x & \bar{p}_x & p_y & \bar{p}_y & p_z & \bar{p}_z \\ \hline p_x & 0 & 0 & -i\,l_z s_z & 0 & 0 & 1\,l_y s_y \\ \bar{p}_x & 0 & 0 & 0 & i\,l_z s_z & -1\,l_y s_y & 0 \\ p_y & i\,l_z s_z & 0 & 0 & 0 & 0 & -i\,l_x s_x \\ \bar{p}_y & 0 & -i\,l_z s_z & 0 & 0 & -i\,l_x s_x & 0 \\ p_z & 0 & -1\,l_y s_y & 0 & i\,l_x s_x & 0 & 0 \\ \bar{p}_z & 1\,l_y s_y & 0 & i\,l_x s_x & 0 & 0 & 0 \end{array} \right) \qquad (12)$$

B. p^5 electron occupancy

In an atom with five filled p orbitals (any halogen, for example) the six definite-m states can be written as

$$P_1 \equiv |p_1 \bar{p}_1 p_0 \bar{p}_0 p_{-1}|$$

$$\bar{P}_1 \equiv |p_1 \bar{p}_1 p_0 \bar{p}_0 \bar{p}_{-1}|$$

$$P_0 \equiv |p_1 \bar{p}_1 p_0 p_{-1} \bar{p}_{-1}|$$

$$\bar{P}_0 \equiv |p_1 \bar{p}_1 \bar{p}_0 p_{-1} \bar{p}_{-1}|$$

$$P_{-1} \equiv |p_1 p_0 \bar{p}_0 p_{-1} \bar{p}_{-1}|$$

$$\bar{P}_{-1} \equiv |\bar{p}_1 p_0 \bar{p}_0 p_{-1} \bar{p}_{-1}|$$

Note that all these six Slater determinants differ from each other by a single spin-orbital replacement. We can rexpress the spin-orbit operator as the the sum of three terms

$$\hat{H}_{so} = \sum_i \hat{a}_i \vec{l}_i \cdot \vec{s}_i = \left(\hat{H}_z + \hat{H}_+ + \hat{H}_- \right)$$

where

$$\hat{H}_z = \sum_i \hat{a}_i l_{zi} s_{zi} \tag{13}$$

$$\hat{H}_+ = \frac{1}{2} \sum_i \hat{a}_i l_{i+} s_{i-} \tag{14}$$

and

$$\hat{H}_- = \frac{1}{2} \sum_i \hat{a}_i l_{i-} s_{i+} \tag{15}$$

or, in the equivalent fully Cartesian representation,

$$\hat{H}_{so} = \sum_i \hat{a}_i \left[l_{xi} s_{xi} + l_{yi} s_{yi} + l_{zi} s_{zi} \right]$$

Now, you can use the rules I gave you for the matrix element of a one-electron operator h between any two Slater determinants which differ in one spin-orbital to determine the matrix of $\hat{H}_{so}$ in the p^5 definite-m. When comparing with the matrix of the spin-orbit operator in the definite-m basis for a p^1 electron occupancy [Eq. (1)], you find that the *diagonal* matrix elements are changed in sign, since, for example

$$\left\langle \bar{P}_1 \right| \hat{H}_{so} \left| \bar{P}_1 \right\rangle = \langle |p_1\bar{p}_1p_0\bar{p}_0\bar{p}_{-1}|| \, \hat{H}_z \, ||p_1\bar{p}_1p_0\bar{p}_0\bar{p}_{-1}| \rangle = \frac{1}{2} - \frac{1}{2} + 0 + 0 + \frac{1}{2} = +\frac{1}{2}$$

The *off-diagonal* matrix elements are rearranged those in Eq. (1), since, for example

$$\left\langle \bar{P}_1 \right| \hat{H}_{so} \left| P_0 \right\rangle = \langle |p_1\bar{p}_1p_0\bar{p}_0\bar{p}_{-1}|| \, \hat{H}_+ \, ||p_1\bar{p}_1p_0p_{-1}\bar{p}_{-1}| \rangle = \langle \bar{p}_0 | \, \hat{H}_+ \, | p_{-1} \rangle$$

However, all the off-diagonal matrix elements in Eq. (1) are the same. Thus, in the definite-m basis, the matrix of the spin-orbit operator for a state of p^5 electron occupancy is

$$\mathbf{H}_{so}^{(m)}(p^5) = \frac{a}{2} \left(\begin{array}{c|cccccc} & P_1 & \bar{P}_1 & P_0 & \bar{P}_0 & P_{-1} & \bar{P}_{-1} \\ \hline P_1 & -1 & 0 & 0 & 0 & 0 & 0 \\ \bar{P}_1 & 0 & 1 & \sqrt{2} & 0 & 0 & 0 \\ P_0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ \bar{P}_0 & 0 & 0 & 0 & 0 & \sqrt{2} & 0 \\ P_{-1} & 0 & 0 & 0 & \sqrt{2} & 1 & 0 \\ \bar{P}_{-1} & 0 & 0 & 0 & 0 & 0 & -1 \end{array} \right) \tag{16}$$

Diagonalization gives eigenvalues of $+a$ (two-fold degenerate) and $-a/2$ (four-fold degenerate), as we would anticipate for a p^5 electron occupancy.

We write the 6 Cartesian states for a p^5 electron occupancy as

$$P_x \equiv |p_xp_y\bar{p}_yp_z\bar{p}_z|$$

$$\bar{P}_x \equiv |\bar{p}_xp_y\bar{p}_yp_z\bar{p}_z|$$

$$P_y \equiv |p_x\bar{p}_xp_yp_z\bar{p}_z|$$

$$\bar{P}_y \equiv |p_x\bar{p}_x\bar{p}_yp_z\bar{p}_z|$$

$$P_z \equiv |p_x\bar{p}_xp_y\bar{p}_yp_z|$$

$$\bar{P}_z \equiv |p_x\bar{p}_xp_y\bar{p}_y\bar{p}_z|$$

The transformation from the six definite-m p^5 spin orbitals to the six Cartesian p^5 spin orbitals is defined similarly to Eq. (7), namely $[\mathbf{T}(p^5)]_{ij} = \langle P_q|\ P_m\rangle$. The full transformation matrix is

$$\mathbf{T}(p^5) = 2^{-1/2}\begin{pmatrix} -1 & 0 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 0 & 1 \\ -i & 0 & 0 & 0 & -i & 0 \\ 0 & -i & 0 & 0 & 0 & -i \\ 0 & 0 & -\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{2} & 0 & 0 \end{pmatrix} \tag{17}$$

Note that the first four rows are identical to the comparable transformation matrix for a p^1 electron occupancy. The last two rows are reversed. Why is this? Consider the 4th Cartesian state $|p_x\bar{p}_x p_y\bar{p}_y p_z|$. Using Eqs. (2) – (4) to convert into definite-m orbitals gives

$$|p_x\bar{p}_x p_y\bar{p}_y p_z| = 2^2 i^2 |(-p_1 + p_{-1})(-\bar{p}_1 + \bar{p}_{-1})(p_1 + p_{-1})(\bar{p}_1 + \bar{p}_{-1})p_0|$$

We now expand, deleting all determinants in which two or more spin-orbitals are identical, to get

$$\begin{aligned} |p_x\bar{p}_x p_y\bar{p}_y p_z| = -\frac{1}{4}\,(&|p_1\bar{p}_1 p_{-1}\bar{p}_{-1} p_z| + |p_{-1}\bar{p}_{-1} p_1\bar{p}_1 p_z| \\ -\ &|p_1\bar{p}_{-1} p_{-1}\bar{p}_1 p_z| - |p_{-1}\bar{p}_1 p_1\bar{p}_{-1} p_z|) \end{aligned}$$

The last three determinants can be rearranged, with a sign change for an odd number of permutations, to yield

$$|p_x\bar{p}_x p_y\bar{p}_y p_z| = -|p_1\bar{p}_1 p_{-1}\bar{p}_{-1} p_z|$$

or

$$P_z = -P_0$$

which explains the negative sign in the last two rows of the $\mathbf{T}(p^5)$ matrix.

Thus, in the basis of the six Cartesian p^5 states, the matrix of the spin-orbit Hamiltonian is

$$\mathbf{H}_{so}^{(q)}(p^5) = \mathbf{T}\,\mathbf{H}_{so}^{(m)}(p^5)\,\mathbf{T}^{\dagger} = \frac{a}{2}\left(\begin{array}{c|cccccc} & P_x & \bar{P}_x & P_y & \bar{P}_y & P_z & \bar{P}_z \\ \hline P_x & 0 & 0 & i\,l_z s_z & 0 & 0 & -1\,l_y s_y \\ \bar{P}_x & 0 & 0 & 0 & -i\,l_z s_z & 1\,l_y s_y & 0 \\ P_y & -i\,l_z s_z & 0 & 0 & 0 & 0 & i\,l_x s_x \\ \bar{P}_y & 0 & i\,l_z s_z & 0 & 0 & i\,l_x s_x & 0 \\ P_z & 0 & 1\,l_y s_y & 0 & -i\,l_x s_x & 0 & 0 \\ \bar{P}_z & -1\,l_y s_y & 0 & -i\,l_x s_x & 0 & 0 & 0 \end{array}\right) \tag{18}$$

Note that this is the *negative* of the matrix in the Cartesian p^1 basis [Eq. (**??**)]. Thus the effect of the spin-orbit interaction is reversed when moving from the left to the right of the periodic table. This matrix is identical to what we would obtain from an *ab initio* calculation on a p^5 atom, as, for example, the calculation on the F atom defined by the Molpro input file `f_so.com`.

The eigenvalues of $\hat{H}_{so}$ are $-a$ and $+a/2$ for a p^1 electron occupancy and $+a$ and $-a/2$ for a p^5 electron occupancy.

You probably have seen the following simplified treatment of spin-orbit coupling: For both a p^1 and p^5 electron occupancy, the sums of the projection quantum numbers of the electron orbital angular momenta are 1, 0, or –1, and the sum of the projection quantum numbers of the electron spin angular momenta of the electrons are +1/2 and –1/2. Thus, the vector sum of the individual electron orbital angular momenta $\vec{L} = \sum \vec{l}_i$ has magnitude 1 and the vector sum of the individual electron spin angular momenta $\vec{S} = \sum \vec{s}_i$ has magnitude 1/2. Consequently, if one vector couples $\vec{L}$ and $\vec{S}$ to obtain the total angular momentum $\vec{J}$, one finds $J = 1/2$ or $3/2$.

One then assumes that the spin-orbit interaction can be written as

$$\hat{H}_{so} = A\vec{L} \cdot \vec{S}$$

where A is an effective spin-orbit constant. Since $\vec{J} = \vec{L} + \vec{S}$

$$\hat{J}^2 = \left(\hat{L} + \hat{S}\right)^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L} \cdot \hat{S}$$

Thus

$$\hat{L} \cdot \hat{S} = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)$$

or

$$\left\langle \hat{H}_{so} \right\rangle = \frac{A}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

This equals $A/2$ for $J = 3/2$ and $-A$ for $J = 1/2$. Comparing this with the eigenvalues of Eqs. (10) and (**??**), we conclude that the effective spin-orbit constant A is $+a$ for a p^1 electron occupancy and $-a$ for a p^5 electron occupancy. Thus the effective spin-orbit constant changes from positive to negative as one moves from the left side to the right side of the periodic table

In reality, the constant a is just the expectation value of the one-electron operator $\hat{a}$ which, as discussed earlier, is proportional to r^{-3}, where r is the distance between the electron on the nucleus. Since the expectation value of r^{-3} can never be negative, the constant a can never be negative. The change in sign of the spin-orbit interaction is a consequence of the subtleties of the different determinantal wavefunctions for a p^1 and p^5 electron occupancy, and, hence, a consequence of the fermion character of the electron!

Since the electron cloud is more tightly bound as one moves across the periodic table, one would expect the F $2p$ orbitals to be closer to the nucleus than those for B. Thus we would anticipate that the expectation value of r^{-3} to be larger for F than for B and, hence, the magnitude of the spin-orbit coupling constant a. The calculations defined by the Molpro input files `b_so.com` and `f_so.com` predict values of 4.50 cm^{-1} and 124.52 cm^{-1} for the ^2P states of B and F, respectively. Although these input files represent calculations with very small (vdz) basis sets, the corresponding experimental valuesof 5.06 and 134.7 cm^{-1} are quite to the predictions.

C. p^2 electron occupancy

For an atom with a p^2 electron occupancy, there are three possible electronic states: ^3P, ^1D, and ^1S. We shall consider first spin-orbit coupling in the ^3P state.

1. Spin-orbit coupling within the ^3P state

In a Slater determinantal notation there are 9 possible projection states, corresponding to $M_S = 0, \pm 1$ and $M_L = 0, \pm 1$.

	$M_S = 1$	0	-1
$M_L = 1$	$\vert p_1 p_0 \vert$	$2^{-1/2}\left[\vert p_1 \bar{p}_0 \vert + \vert \bar{p}_1 p_0 \vert\right]$	$\vert \bar{p}_1 \bar{p}_0 \vert$
-1	$\vert p_0 p_{-1} \vert$	$2^{-1/2}\left[\vert p_0 \bar{p}_{-1} \vert + \vert \bar{p}_0 p_{-1} \vert\right]$	$\vert \bar{p}_0 \bar{p}_{-1} \vert$
0	$\vert p_1 p_{-1} \vert$	$2^{-1/2}\left[\vert p_1 \bar{p}_{-1} \vert + \vert \bar{p}_1 p_{-1} \vert\right]$	$\vert \bar{p}_1 \bar{p}_{-1} \vert$

(19)

We will order these definite-m states row-wise, starting from the $M_L = 1$ and moving first through the values of M_S, in other words

	$M_S = 1$	0	-1
$M_L = 1$	1	2	3
-1	4	5	6
0	7	8	9

(20)

To determine the matrix of the spin-orbit operator in the definite-m basis,

$$\langle \Phi' | \hat{H}_{so} | \Phi \rangle = \langle \Phi' | \hat{H}_z | \Phi \rangle + \langle \Phi' | \hat{H}_+ | \Phi \rangle + \langle \Phi | \hat{H}_- | \Phi' \rangle$$

we proceed as follows:

We shall work within the definite-m basis, in which case states $|\Phi\rangle$ and $|\Phi'\rangle$ can be represented as a Slater determinant containing two (or, in general, several) spin-orbitals which are eigenfunctions of l_z and s_z.

(a) Suppose the Slater determinants are identical. Since the raising and lower operators change any $|l m_l s m_s\rangle$ spin-orbital into a different spin-orbital, $\hat{H}_\pm |\Phi\rangle$ will be orthogonal to $\langle \Phi|$ so that $\langle \Phi | \hat{H}_\pm | \Phi \rangle$ will vanish. Thus the matrix element will be due entirely to the $\hat{H}_z$ operator, with the result

$$\langle \Phi | \hat{H}_{so} | \Phi \rangle = \langle \Phi | \hat{H}_z | \Phi \rangle = \sum_i \langle p_i | l_z s_z | p_i \rangle = \sum_i m_{l_i} m_{s_i}$$

(b) Suppose the Slater determinants differ by one spin orbital. Let us designate this spin orbital as $\phi_{m_l' m_s'}$ in the determinant Φ' and $\phi_{m_l m_s}$ in the determinant Φ. Since matrix element of any one-electron operator $\hat{A}$ between two Slater determinants which differ by one spin-orbital is

$$\langle \Phi' | \hat{A} | \Phi \rangle = \left\langle \phi_{m_l' m_s'} \right| \hat{A} \left| \phi_{m_l m_s} \right\rangle$$

we have

$$\langle \Phi' | \hat{H}_{so} | \Phi \rangle = \left\langle \phi_{m_l' m_s'} \right| \hat{H}_z + \hat{H}_+ + \hat{H}_- \left| \phi_{m_l m_s} \right\rangle \tag{21}$$

Because the spin-orbitals ϕ and ϕ' differ, but are both eigenfunctions of $\hat{l}_z$ and $\hat{s}_z$, the matrix element of the operator $\hat{H}_z$ will be zero. Thus we have

$$\langle \Phi' | \hat{H}_{so} | \Phi \rangle = \frac{a}{2} \left[l(l+1) + m_l(m_l \mp 1) \right]^{1/2} \delta_{m_{l'}, m_l \pm 1} \delta_{m_{s'}, m_s \mp 1}$$

Specifically, in the case of p orbitals, the only non-zero matrix elements are

$$\langle \bar{p}_m | H_+ | p_{m-1} \rangle = \langle p_{m-1} | H_- | \bar{p}_m \rangle = 2^{-1/2} a \,,$$

for $m = 1$ and $m = 0$. Here we also assume that the matrix element of $\hat{a}$, which depends on only the spatial coordinates of the electron, is independent of orientation and thus independent of the projection quantum number. We shall designate by a (no hat) the value of this matrix element.

(c) Suppose the Slater determinants for Φ and Φ' differ by two (or, in general, two or more) spin-orbitals. Then the matrix element vanishes, since $\hat{H}_{so}$ is a one-electron operator.

For example, consider the matrix element of the spin-orbit operator between states $|7\rangle = |p_1 p_{-1}|$ and $|2\rangle = 2^{-1/2} \left(|p_1 \bar{p}_0| + |\bar{p}_1 p_0| \right)$. Since these determinants differ in the second spinorbital, only H_+ and H_- will contribute. We have

$$\begin{aligned} \langle 7 | \hat{H}_+ + \hat{H}_- | 2 \rangle &= \langle |p_1 p_{-1}| | \hat{H}_z \left[2^{-1/2} \left(|p_1 \bar{p}_0| + |\bar{p}_1 p_0| \right) \right] \\ &= \langle |p_1 p_{-1}| | \hat{H}_- \left| 2^{-1/2} |p_1 \bar{p}_0| \right\rangle + 0 = 2^{-1/2} \frac{a}{2} \langle p_{-1} | l_- s_+ | \bar{p}_0 \rangle = a/2 \end{aligned} \tag{22}$$

Similarly, consider the diagonal matrix element $\langle 4 | \hat{H}_{so} | 4 \rangle = \langle |p_0 p_{-1}| | \hat{H}_{so} | |p_0 p_{-1}| \rangle$. Since this is a diagonal matrix element, only the operator $\hat{H}_z$ will contribute, giving

$$\langle |p_0 p_{-1}| | \hat{H}_z | |p_0 p_{-1}| \rangle = a \left(0 \times \frac{1}{2} - 1 \times \frac{1}{2} \right) = -a/2$$

The full matrix of the spin-orbit operator in the definite-m basis is then

$$\mathbf{H}_{so}^{(m)} = \frac{a}{2} \left(\begin{array}{ccc|ccccccccc} & & M_L & 1 & 1 & 1 & -1 & -1 & -1 & 0 & 0 & 0 \\ & & M_S & 1 & 0 & -1 & 1 & 0 & -1 & 1 & 0 & -1 \\ M_L & M_S & M_J & 2 & 1 & 0 & 0 & -1 & -2 & 1 & 0 & -1 \\ \hline 1 & 1 & 2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 \\ -1 & 1 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & -1 & -2 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{array} \right) \tag{23}$$

The eigenvalues of the matrix in Eq. (23) are $-a$ (singly degenerate), $-a/2$ (triply denegerate) and $+a/2$ (five-fold degenerate). Let us define the sum of the orbital and spin projection quantum numbers by upper case M_L and M_S, namely,

$$M_L = m_{l1} + m_{l2}$$

and

$$M_S = m_{s1} + m_{s2}$$

as well as the total projection quantum number

$$M_J = M_L + M_S = m_{l1} + m_{l2} + m_{s1} + m_{s2}$$

We then notice that the off-diagonal matrix elements, which arise from the $\hat{H}_+$ and $\hat{H}_-$ terms, vanish unless $M'_L + M'_S = M_L + M_S$ (in other words, unless the projection quantum number of the total angular momentum M_J is unchanged), and, even when this "selection" rule is satisfied, unless $M'_L = M_L \pm 1$ while, simultaneously, $M'_S = M_S \mp 1$.

Alternatively, one can define 9 Cartesian states, which we define as

	$M_S = 1$	0	-1
xz	$\lvert p_x p_z \rvert$	$2^{-1/2}\left[\lvert p_x \bar{p}_z \rvert + \lvert \bar{p}_x p_z \rvert\right]$	$\lvert \bar{p}_x \bar{p}_z \rvert$
yz	$\lvert p_y p_z \rvert$	$2^{-1/2}\left[\lvert p_y \bar{p}_z \rvert + \lvert \bar{p}_y p_z \rvert\right]$	$\lvert \bar{p}_y \bar{p}_z \rvert$
xy	$\lvert p_x p_y \rvert$	$2^{-1/2}\left[\lvert p_x \bar{p}_y \rvert + \lvert \bar{p}_x p_y \rvert\right]$	$\lvert \bar{p}_x \bar{p}_y \rvert$

(24)

We will order the Cartesian states similarly to Eq. (38), in other words

	$M_S = 1$	0	-1
xz	1	2	3
yz	4	5	6
xy	7	8	9

(25)

From Eqs. (2)–(4), it is easy to show that the transformation from the definite-m to the Cartesian basis is

$$\mathbf{T} = 2^{-1/2} \begin{pmatrix} -\mathbf{I} & -\mathbf{I} & \mathbf{0} \\ -i\mathbf{I} & i\mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & i\sqrt{2}\mathbf{I} \end{pmatrix} \tag{26}$$

where $\mathbf{0}$ is a 3×3 nul matrix and $\mathbf{1}$ is a 3×3 identity matrix. In deriving the expression for this transformation matrix you have to be careful of phases. For example,

$$\begin{aligned} T_{14} &= \langle \lvert p_x p_z \rvert \lvert p_0 p_{-1} \rvert \rangle = 2^{-1/2} \langle (-\lvert p_1 p_0 \rvert + \lvert p_{-1} p_0 \rvert) \, \lvert p_0 p_{-1} \rvert \rangle \\ &= -2^{-1/2} \langle (-\lvert p_1 p_0 \rvert + \lvert p_{-1} p_0 \rvert) \, \lvert p_{-1} p_0 \rvert \rangle = -2^{-1/2} \,, \end{aligned}$$

and

$$\begin{aligned} T_{44} &= \langle \lvert p_y p_z \rvert \lvert p_0 p_{-1} \rvert \rangle = 2^{-1/2} \langle (i \lvert p_1 p_0 \rvert + i \lvert p_{-1} p_0 \rvert)^* \, \lvert p_0 p_{-1} \rvert \rangle = -2^{-1/2} i \langle (\lvert p_1 p_0 \rvert + \lvert p_{-1} p_0 \rvert) \, \lvert p_0 p_{-1} \rvert \rangle \\ &= +2^{-1/2} i \langle (\lvert p_1 p_0 \rvert + \lvert p_{-1} p_0 \rvert) \, \lvert p_{-1} p_0 \rvert \rangle = +2^{-1/2} i \,, \end{aligned}$$

and

$$T_{77} = \langle \lvert p_x p_y \rvert \lvert p_1 p_{-1} \rvert \rangle = 2^{-1} \, \langle (-i \lvert p_1 p_{-1} \rvert + i \lvert p_{-1} p_1 \rvert)^* \, \lvert p_1 p_{-1} \rvert \rangle = +i$$

Similarly to Eq. (8) we can use the matrix of the spin-orbit operator in the definite-m

basis to derive an expression for the matrix of the spin-orbit operator in the Cartesian basis. With the state-ordering defined by Eq. (25) we find

$$\mathbf{H}_{so}^{(q)}(p^2) = \mathbf{T}\mathbf{H}_{so}^{(m)}(p^2)\mathbf{T}^{\dagger} = 2^{-3/2}a \begin{pmatrix} 0 & 0 & 0 & -i\sqrt{2} & 0 & 0 & 0 & i & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & i & 0 & i \\ 0 & 0 & 0 & 0 & 0 & i\sqrt{2} & 0 & i & 0 \\ i\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 \\ 0 & 0 & -i\sqrt{2} & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & -i & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ -i & 0 & -i & 1 & 0 & -1 & 0 & 0 & 0 \\ 0 & -i & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{27}$$

As can be seen in the output of the Molpro input file `c_3p_so.com`, the calculated matrix of the spin-orbit operator agrees identically with the one derived in Eq. (27).

2. *Spin-orbit coupling between the ^3P and ^1D states*

As a final topic in the discussion of spin-orbit coupling in atoms, we cansider the spin-orbit induced mixing between the ^3P and ^1D states arising from a p^2 electron occupancy.

For the ^1D state of an atom with a p^2 electronic configuration, there are five projection states,

$M_L = 2$	$\lvert p_1\bar{p}_1\rvert$
1	$2^{-1/2}\left[\lvert p_1\bar{p}_0\rvert + \lvert p_0\bar{p}_1\rvert\right]$
0	$6^{-1/2}\left[2\lvert p_0\bar{p}_0\rvert + \lvert p_{-1}\bar{p}_1\rvert + \lvert p_1\bar{p}_{-1}\rvert\right]$
-1	$2^{-1/2}\left[\lvert p_{-1}\bar{p}_0\rvert + \lvert p_0\bar{p}_{-1}\rvert\right]$
-2	$\lvert p_{-1}\bar{p}_{-1}\rvert$

(28)

The wavefunctions for each M_L can obtained from the wavefunction for the state with $M_L + 1$ by operating with the projection operator $\hat{L}_- = \hat{l}_{1-} + \hat{l}_{2-}$. The matrix elements for the spin-orbit operator between these 5 states and the 9 ^3P states in the definite-m basis can be obtained using the selection rules we found in Eq. (23), namely $M_S' = M_S \pm 1$, $M_L' = M_L \mp 1$. If we label these states $|10\rangle$–$|14\rangle$, then the matrix of $\hat{H}_{so} + \hat{H}_{el}$in the combined basis of the 9 definite-m ^3P states plus the five definite-m ^2D states is

$$\mathbf{H}_{el}^{(m)}(^3P/^1D) + \mathbf{H}_{so}^{(m)}(^3P/^1D) = E(^3P)\mathbf{1} + \begin{pmatrix} \mathbf{H}_{so}^{(m)}(^3P) & \mathbf{H}_{13}^{(m)} \\ \left[\mathbf{H}_{13}^{(m)}\right]^T & \mathbf{\Delta E} \end{pmatrix} \tag{29}$$

where $\mathbf{H}_{so}^{(m)}(^3P)$ is given by Eq. (23), $\mathbf{1}$ is a 14×14 unit matrix, $\mathbf{\Delta E}$ is a 5×5 diagonal matrix with elements equal to the difference between the energies of the ^3P and ^1D states, namely

$$\mathbf{\Delta E}_{ij} = \delta_{ij}\left[E(^1D) - E(^3P)\right] ,$$

and $\mathbf{H}_{31}$ is the 9×5 matrix (in red are the terms in the spin-orbit Hamiltonian [Eqs. (13), (14) and (15)] which provide the coupling for the various non-zero $\langle ^3P|\, H_{so}\, |^1D\rangle$ matrix elements).

$$\mathbf{H}_{31}^{(m)} = \frac{a_{13}}{2} \left(\begin{array}{ccc|ccccc} & & M_L & 2 & 1 & 0 & -1 & -2 \\ & & M_S & 0 & 0 & 0 & 0 & 0 \\ M_L & M_S & M_J & 2 & 1 & 0 & -1 & -2 \\ \hline 1 & 1 & 2 & \sqrt{2}, H_- & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1, H_z & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & \sqrt{1/3}, H_+ & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 & \sqrt{1/3}, H_- & 0 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 1, H_z & 0 \\ -1 & -1 & -2 & 0 & 0 & 0 & 0 & \sqrt{2}, H_+ \\ 0 & 1 & 1 & 0 & 1, H_- & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{4/3}, H_z & 0 & 0 \\ 0 & -1 & -1 & 0 & 0 & 0 & 1, H_+ & 0 \end{array} \right) \tag{30}$$

To obtain the matrix elements in Eq. (30) we can use the same approach as used earlier for the determination of the spin-orbit matrix elements within the C(^3P) state [Eq. 21] but here with the definite-m Slater determinantal wavefunctions for both the ^3P and the ^1D state [Eq. (28)]. As before, the matrix elements vanish unless $M_L' = M_L$ and $M_S' = M_S$ or unless $M_L' = M_L \pm 1$ and $M_S' = M_S \mp 1$. Note that we have designated the spin-orbit coupling constant as a_{13}. Because both the ^1D and ^3P states have the same $1s^2 2s^2 2p^2$

electron occupancy, the magnitude of the spin-orbit constant should be very similar. As will be seen below, in an actual calculation, the constants are the same at the level of the mean-field approximation, [1] but slight differences occur when the full Breit-Pauli Hamiltonian is used.

To illustrate the process, consider the second ^3P state, namely $2^{-1/2}\left[|p_1\bar{p}_0| + |\bar{p}_1 p_0|\right]$, and the second ^1D state, namely $2^{-1/2}\left[|p_1\bar{p}_0| + |p_0\bar{p}_1|\right]$. Since the same spin-orbitals are occupied in both states, only the $\bar{H}_z$ operator will contribute. To make things easier, we reorder the 2nd determinant in the expression for state $2(^3P)$ as

$$\left|2(^3P)\right\rangle = 2^{-1/2}\left[|p_1\bar{p}_0| - |p_0\bar{p}_1|\right]$$

We then find

$$\begin{aligned}\left\langle 2(^3P)\right| \hat{H}_z \left|2(^1D)\right\rangle &= \left\langle M_L = 1, M_S = 0;\, ^3P\right| \hat{H}_z \left|M_L = 1, M_S = 0;\, ^1D\right\rangle \\ &= \frac{a}{2}\Big[\langle |p_1\bar{p}_0|| \,\hat{H}_z\, ||p_1\bar{p}_0|\rangle - \langle |p_1\bar{p}_0|| \,\hat{H}_z\, ||p_0\bar{p}_1|\rangle \\ &\quad + \langle |p_0\bar{p}_1|| \,\hat{H}_z\, ||p_1\bar{p}_0|\rangle - \langle |p_0\bar{p}_1|| \,\hat{H}_z\, ||p_0\bar{p}_1|\rangle\Big] \\ &= \frac{a}{2}\left[1/2 - 0 + 0 - (-1/2)\right] = a/2 \qquad (31)\end{aligned}$$

Similarly, you can show that

$$\left\langle 5(^3P)\right| \hat{H}_z \left|4(^1D)\right\rangle = \left\langle M_L = -1, M_S = 0;\, ^3P\right| \hat{H}_z \left|M_L = -1, M_S = 0;\, ^1D\right\rangle = a/2\,, \qquad (32)$$

$$\left\langle 8(^3P)\right| \hat{H}_z \left|3(^1D)\right\rangle = \left\langle M_L = 0, M_S = 0;\, ^3P\right| \hat{H}_z \left|M_L = 0, M_S = 0;\, ^1D\right\rangle = a/\sqrt{3} \qquad (33)$$

and,

$$\left\langle 7(^3P)\right| \hat{H}_z \left|2(^1D)\right\rangle = \left\langle M_L = 0, M_S = 1;\, ^3P\right| \hat{H}_z \left|M_L = -1, M_S = 0;\, ^1D\right\rangle = a/2 \qquad (34)$$

We shall define the five Cartesian ${}^1D$ states by the 2nd column of the following table.

	Determinantal notation	
state	Cartesian	definite$-m$
x^2-y^2	$2^{-1/2}\,[\lvert p_x\bar{p}_x\rvert - \lvert p_y\bar{p}_y\rvert]$	$2^{-1/2}\,[\lvert p_1\bar{p}_1\rvert + \lvert p_{-1}\bar{p}_{-1}\rvert]$
$2z^2-x^2-y^2$	$6^{-1/2}\,[2\lvert p_z\bar{p}_z\rvert - \lvert p_x\bar{p}_x\rvert - \lvert p_y\bar{p}_y\rvert]$	$6^{-1/2}\,[2\lvert p_0\bar{p}_0\rvert + \lvert p_1\bar{p}_{-1}\rvert + \lvert p_{-1}\bar{p}_1\rvert]$
xy	$2^{-1/2}\,[-\lvert p_x\bar{p}_y\rvert + \lvert \bar{p}_x p_y\rvert]$	$i2^{-1/2}\,[\lvert p_1\bar{p}_1\rvert - \lvert p_{-1}\bar{p}_{-1}\rvert]$
zx	$2^{-1/2}\,[-\lvert p_z\bar{p}_x\rvert + \lvert \bar{p}_z p_x\rvert]$	$\frac{1}{2}\,[-\lvert p_1\bar{p}_0\rvert - \lvert p_0\bar{p}_1\rvert + \lvert p_0\bar{p}_{-1}\rvert + \lvert p_{-1}\bar{p}_0\rvert]$
yz	$2^{-1/2}\,[-\lvert p_y\bar{p}_z\rvert + \lvert \bar{p}_y p_z\rvert]$	$-\frac{i}{2}\,[\lvert p_1\bar{p}_0\rvert + \lvert p_0\bar{p}_1\rvert + \lvert p_0\bar{p}_{-1}\rvert + \lvert p_1\bar{p}_0\rvert]$

(35)

These definitions correspond to the definitions of the real spherical harmonics for $l = 2$. You should notice that the relative signs of the two Slater determinants in the Cartesian representation of the xy, zx, and yz states is dictated by the requirement that these $M_S = 0$ states (which are components of the ${}^1D$ state) be orthogonal to the corresponding $M_S = 0$ components of the ${}^3P$ state given in (24).

If we use the definitions of the Cartesian ${}^1D$ states given in (35), and the definition of the definite-m ${}^1D$ states in (28), then we obtain the representation of the Cartesian ${}^1D$ states in terms of the definite-m states which is given in the 3rd column of (35). The matrix $T({}^1D)$ which transforms from the definite-m to Cartesian ${}^1D$ states is

$$\mathbf{T}({}^1D) = 2^{-1/2}\begin{pmatrix} 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & \sqrt{2} & 0 & 0 \\ i & 0 & 0 & 0 & -i \\ 0 & -1 & 0 & 1 & 0 \\ 0 & -i & 0 & -i & 0 \end{pmatrix}$$

Thus, for the combined ${}^3P/{}^1D$ basis, the matrix $\mathbf{T}$ which transforms from the definite-m to Cartesian basis is

$$\mathbf{T}({}^3P/{}^1D) = \begin{pmatrix} \mathbf{T}({}^3P) & \mathbf{0}_{31} \\ \mathbf{0}_{31}^T & \mathbf{T}({}^1D) \end{pmatrix}$$

where $\mathbf{0}_{31}$ is a 9×5 nul matrix and $\mathbf{T}({}^3P)$ is given by Eq. (26). The resulting matrix of the matrix of $\hat{H}_{so} + \hat{H}_{el}$ in the combined basis of the 9 Cartesian ${}^3P$ states plus the five

Cartesian ^2D states is

$$\mathbf{H}_{el}^{(q)}(^3P/^1D) + \mathbf{H}_{so}^{(q)}(^3P/^1D) = E(^3P)\mathbf{1} + \begin{pmatrix} \mathbf{H}_{so}^{(q)}(^3P) & \mathbf{H}_{13}^{(q)} \\ \left[\mathbf{H}_{13}^{(q)}\right]^{\dagger} & \Delta\mathbf{E} \end{pmatrix}$$

where $\mathbf{H}_{so}^{(q)}(^3P)$ is given by Eq. (27) and

$$\mathbf{H}_{13}^{(q)} = a_{13} \begin{pmatrix} -1/\sqrt{2} & -1/\sqrt{6} & i/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -i \\ -1/\sqrt{2} & -1/\sqrt{6} & -i/\sqrt{2} & 0 & 0 \\ -i/\sqrt{2} & i/\sqrt{6} & -1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & i & 0 \\ i/\sqrt{2} & -i/\sqrt{6} & -1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & -i/\sqrt{2} & -1/\sqrt{2} \\ 0 & i\sqrt{4/3} & 0 & 0 & 0 \\ 0 & 0 & 0 & i/\sqrt{2} & -1/\sqrt{2} \end{pmatrix}$$

These agrees with the output of the Molpro input file `c_3p_1d_so.com`. This agreement is further confirmation of the choice we have made of relative signs in the determinantal wavefunctions which make up the five ^1D Cartesian states in the Table on page 20, which was also guided by the known definition of the real spherical harmonics for $l = 2$.

D. Symmetry blocking

We discussed in connection with the matrices in Eqs. (23) and (30) that the spin-orbit operator will couple only states with the same value of $M_J = M_L + M_S$. Thus, if we reorder the nine definite-m $p^2(^3P)$ states as

M_J	M_L	M_S	n	determinant
2	1	1	1	$\lvert p_1 p_0\rvert$
1	1	0	2	$2^{-1/2}\left[\lvert p_1\bar{p}_0\rvert + \lvert\bar{p}_1 p_0\rvert\right]$
1	0	1	3	$\lvert p_1 p_{-1}\rvert$
0	1	-1	4	$\lvert\bar{p}_1\bar{p}_0\rvert$
0	0	0	5	$2^{-1/2}\left[\lvert p_1\bar{p}_{-1}\rvert + \lvert\bar{p}_1 p_{-1}\rvert\right]$
0	-1	1	6	$\lvert p_0 p_{-1}\rvert$
-1	0	-1	7	$\lvert\bar{p}_1\bar{p}_{-1}\rvert$
-1	-1	0	8	$2^{-1/2}\left[\lvert p_0\bar{p}_{-1}\rvert + \lvert\bar{p}_0 p_{-1}\rvert\right]$
-2	-1	-1	9	$\lvert\bar{p}_0\bar{p}_{-1}\rvert$

	$M_S = 1$	0	-1
$M_L = 1$	$\lvert p_1 p_0\rvert$	$2^{-1/2}\left[\lvert p_1\bar{p}_0\rvert + \lvert\bar{p}_1 p_0\rvert\right]$	$\lvert\bar{p}_1\bar{p}_0\rvert$
-1	$\lvert p_0 p_{-1}\rvert$	$2^{-1/2}\left[\lvert p_0\bar{p}_{-1}\rvert + \lvert\bar{p}_0 p_{-1}\rvert\right]$	$\lvert\bar{p}_0\bar{p}_{-1}\rvert$
0	$\lvert p_1 p_{-1}\rvert$	$2^{-1/2}\left[\lvert p_1\bar{p}_{-1}\rvert + \lvert\bar{p}_1 p_{-1}\rvert\right]$	$\lvert\bar{p}_1\bar{p}_{-1}\rvert$

(36)

$$H_{so}^{(m,s)} = \frac{a}{2}\left(\begin{array}{cc||c|cc|ccc|cc|c}
 & n & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\
n' & M_{J'}\backslash M_J & 2 & 1 & 1 & 0 & 0 & 0 & -1 & -1 & -2 \\
\hline\hline
1 & 2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
2 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
3 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
4 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\
5 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\
6 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 \\
\hline
7 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
8 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
\hline
9 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{array}\right)$$

E. p^4 electron occupancy

For an atom with a p^4 electron occupancy, as with an atom with a p^2 electron occupancy, there are three possible electronic states: ${}^3P$, ${}^1D$, and ${}^1S$. We shall consider here only spin-orbit coupling in the ${}^3P$ state.

1. *Spin-orbit coupling within the ${}^3P$ state*

In a Slater determinantal notation there are 9 possible projection states, corresponding to $M_S = 0, \pm 1$ and $M_L = 0, \pm 1$.

	$M_S = 1$	0	-1
$M_L = 1$	$\lvert p_1 \bar{p}_1 p_0 p_{-1} \rvert$	$2^{-1/2}\left[\lvert p_1 \bar{p}_0 \rvert + \lvert \bar{p}_1 p_0 \rvert\right]$	$\lvert p_1 \bar{p}_1 \bar{p}_0 \bar{p}_{-1} \rvert$
-1	$\lvert p_0 p_{-1} \rvert$	$2^{-1/2}\left[\lvert p_0 \bar{p}_{-1} \rvert + \lvert \bar{p}_0 p_{-1} \rvert\right]$	$\lvert \bar{p}_0 \bar{p}_{-1} \rvert$
0	$\lvert p_1 p_{-1} \rvert$	$2^{-1/2}\left[\lvert p_1 \bar{p}_{-1} \rvert + \lvert \bar{p}_1 p_{-1} \rvert\right]$	$\lvert \bar{p}_1 \bar{p}_{-1} \rvert$

(37)

We will order these definite-m states row-wise, starting from the $M_L = 1$ and moving first through the values of M_S, in other words

	$M_S = 1$	0	-1
$M_L = 1$	1	2	3
-1	4	5	6
0	7	8	9

(38)

[1] B. A. Hess, C. M. Marian, U. Wahlgren, and O. Gropen, Chem. Phys. Lett. **251**, 365 (1996).