Relativistic Potential Energy Surfaces of XH2 (X=C, Si, Ge, Sn, and Pb) Molecules: Coupling of 1 A 1 and 3 B 1 States

Nikita Matsunaga
_Iowa State University_

Shiro Koseki
_Mie University_

Mark S. Gordon
_Iowa State University_, mgordon@iastate.edu

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Abstract
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Keywords
Potential energy surfaces, Elemental semiconductors, Germanium, Lead, Ab initio calculations

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Comments
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Relativistic potential energy surfaces of XH$_2$ (X=C, Si, Ge, Sn, and Pb) molecules: Coupling of $^1A_1$ and $^3B_1$ states

Nikita Matsumura
Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

Shiro Koseki
Department of Chemistry, Faculty of Education, Mie University, Tsu, 514, Japan

Mark S. Gordon
Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

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Potential energy surfaces of the $^1A_1$ and $^3B_1$ states for XH$_2$ molecules (X=C, Si, Ge, Sn, Pb) are investigated with ab initio full valence multiconfigurational self-consistent field wave functions, using effective core potentials. Spin–orbit coupling is also calculated to construct relativistic potential energy surfaces. The relativistic potential energy surfaces are compared with the adiabatic nonrelativistic potentials. Simple one dimensional Landau–Zener transition probabilities are calculated at the minimum energy crossing points of XH$_2$ molecules to estimate the intersystem crossing probability. © 1996 American Institute of Physics. [S0021-9606(96)03018-7]

INTRODUCTION

Spin–orbit coupling is the major mechanism that connects two adiabatic potential energy surfaces of different spin. This coupling arises due to the interaction between the spin magnetic moment and the orbital motion of an electron around a nucleus. It lifts the degeneracy of a triplet state, for example, into three substates, and with correct symmetries of the spatial and spin parts of the wave function these two states may couple. Spin–orbit coupled states should then give a more realistic view of potential energy surfaces, and it is certainly essential to include spin–orbit coupling in a calculation of potential energy surfaces (PES) of molecules containing heavy elements. For example, one could not possibly obtain even a qualitatively correct dissociation curve of CH$_2$I$^1$, due to the spin–orbit splitting of iodine into $^3P_{1/2}$ and $^3P_{3/2}$.

Although the formalism for evaluating spin–orbit coupling matrix elements is available for molecular calculations, there are still a limited number of such calculations, especially as applied to potential energy surfaces or chemical reactions of polyatomic molecules.

The effective core potential (ECP) method that projects out core-electron contributions is a powerful way to include heavier elements in calculations on large systems. We have successfully applied ECP’s to a number of systems, including main-group and transition metal complexes. The ECP method has also been used in the calculations of spin–orbit coupling in order to avoid the rather large computational expense in studying heavy element containing molecules.

The spin–orbit coupling of two different spin states is determined by using a relativistic Breit–Pauli Hamiltonian. Recently, we have utilized the one-electron Breit–Pauli Hamiltonian and systematically deduced the effective nuclear charges of second and third period main group elements using an all-electron basis set. We also reported the effective nuclear charges derived from effective core potentials developed by Stevens et al. for second to fifth period alkaline earth and main group elements.

Another method utilizing ECP’s to calculate spin–orbit integrals is due to Ermle et al. These authors have noted that the differences between the two $j$-dependent relativistic effective potentials, obtained by fitting the atomic full relativistic Dirac–Hartree–Fock calculations, corresponds to the spin–orbit operator in the core region. Therefore, the gaussian exponents used in the usual ECP integral calculations can be used to define a spin–orbit operator for the core space.

CH$_2$ is unique among the group IV XH$_2$ molecules, in that the ground state is a triplet state. The experimental singlet–triplet splitting is in the range 8.5–9.0 kcal/mol. A number of accurate theoretical calculations are also available, in which the calculated singlet–triplet splittings converge close to the experimental values. The lowest singlet state in the remaining group IV A XH$_2$ species is lower in energy than the lowest triplet states. Several theoretical calculations at various levels of theory have been reported for SiH$_2$. The most accurate of these place the singlet–triplet splitting at 19–21 kcal/mol.

There are only a handful of theoretical studies dealing with the singlet–triplet splitting and the stationary points on the PES of GeH$_2$, SnH$_2$, and PbH$_2$. The spin–orbit effects are explicitly treated in some of these studies. Electron diffraction derived structures, although they are not dihydrides [XR$_2$, X=Ge, Sn; R=CH(SiMe$_3$)$_2$] have also been reported. These are the only experimental XH$_2$ related structures for heavier group IV A elements in the gas phase.

The energetics, as well as geometries, are affected by large spin–orbit coupling between singlet and triplet states of the heavier group IV A XH$_2$ compounds. It is certainly interesting to learn how the relativistic PES of XH$_2$ are different from the adiabatic PES. Here we report potential energy surfaces of XH$_2$ (X=C, Si, Ge, Sn, and Pb) possessing $C_{2v}$ symmetry.
symmetry, in which the adiabatic and spin–orbit states of these XH₂ species are compared. The Landau–Zener transition model was also utilized to gain more insight into how transitions between two states might occur.

**COMPUTATIONAL APPROACH**

The potential energy surfaces of the XH₂ species are prepared with full optimized reaction space (FORS) multi-configuration self-consistent field (MCSCF or CASSCF) calculations defined by Ruedenberg et al. The active space is a full valence space, i.e., six electrons are distributed among six orbitals in the active space. These six orbitals correspond to the two bonding and two antibonding XH bonds, X lone pair and X empty p orbital for a singlet state.

Effective core potentials (ECP), which utilize the averaged relativistic core potentials, of Stevens et al. (SBK) are used throughout this paper. Since some of the relativistic effects in the core region, especially contraction of orbitals, are already described with the potentials, geometries obtained with the ECP are expected to be better than those obtained with all-electron basis sets for heavier elements. The lowest singlet (X \(^1\)A₁) and the lowest triplet (A \(^3\)B₁) state potential energy surfaces of XH₂ are constructed for a range of bond distances and bond angles, retaining C₂ᵥ symmetry.

Spin–orbit coupling is calculated by using the one-electron part of the microscopic Breit–Pauli Hamiltonian,

\[
H_{SO} = \frac{e^2 \hbar}{2m_e c} \sum_{i,\alpha} \frac{Z_{\text{eff}}^i}{r_{\alpha i}} \left( \mathbf{r}_{\alpha i} \times \mathbf{p}_i \right) \cdot \mathbf{s}_i,
\]

where \(i\) runs over all electronic coordinates and \(\alpha\) runs over all nuclear centers. \(Z_{\text{eff}}^i\) is an adjustable parameter which is determined systematically by adjusting \(Z_{\text{eff}}\) so that the fine structure splittings of the lowest II states of diatomic hydrides (XH) are reproduced. \(Z_{\text{eff}}\) for carbon, silicon, germanium, and tin are 3.90, 168, 1312, and 5500, respectively. \(Z_{\text{eff}}\) for lead (18200) is chosen to reproduce the fine structure splitting of the Pb atom.

The matrix elements are calculated using the Breit–Pauli spin–orbit operator in Eq. (1), and are placed in a Hamiltonian matrix (4×4 in this case) which is complex. This matrix is diagonalized to obtain the eigenvalues of the four spin-mixed states.

The transition probability is estimated by using a Landau–Zener model for intersystem crossing. The transition probability \(P_{LZ}\) can be given by

\[
1 - P_{LZ} = 1 - e^{-2\delta},
\]

where

\[
\delta = \frac{\pi |H_{ij}|^2}{\hbar |\Delta g_{ij}|},
\]

and where \(H_{ij}\) is the spin–orbit coupling matrix element between two adiabatic states \(i\) and \(j\), \(\nu\) is the velocity with which the system is passing through the singlet–triplet crossing region, and \(\Delta g_{ij}\) is the difference in the gradients of the two adiabatic states \(i\) and \(j\). The transition probability was calculated for a range of kinetic energies.

**RESULTS AND DISCUSSION**

The stationary points on the adiabatic PES and the relativistic PES of XH₂ are compared with available experiments and relativistic Dirac–Hartree–Fock (DHF) calculations in Table I. The bond lengths of adiabatic XH₂ singlet states calculated with the MCSCF/SBK(d,p) level of theory are 0.04–0.07 Å longer than those for the triplet states. Except for CH₂, the bond angle at which the minimum on the adiabatic PES occurs for singlets is \(\approx 90°\), and for triplets the angle is \(\approx 120°\). The geometries obtained from the relativistic PES for SiH₂ and GeH₂ do not differ from the adiabatic PES. This is due to the fact that the spin–orbit coupling is smaller than that in the heavier XH₂ species, even though the position of the crossing seam is closer to the triplet minima of SiH₂ and GeH₂ than to the singlet minima. For CH₂ the adiabatic triplet state crosses right at the position of the singlet minimum on the adiabatic surface. Hence a small change in the singlet state geometry results upon mixing of the states by spin–orbit coupling, even though the spin–orbit coupling in CH₂ is the smallest among the XH₂ molecules in the region where the crossing occurs. The MCSCF/SBK(d,p) bond lengths are longer than the corresponding DHF values.

Since there is no two-electron spin-other-orbit coupling term in the DHF calculation, DHF and MCSCF/SBK(d,p) should be in close agreement, except for the fact that our ECP results contain nondynamical correlation through the MCSCF wave functions. Also, the ECP basis set is constructed so as to reproduce the position of the maximum in the atomic radial wavefunctions taken from the DHF calculations. Therefore, relativistic effects, such as inner-shell contractions, are already included in the ECP. The source of any difference in geometry obtained with MCSCF/SBK(d,p) and the DHF calculations should be the nondynamical correlation.

The calculated bond angles are consistently in better agreement with other ab initio calculations, than the bond lengths, except for PbH₂, in which both geometrical parameters are not in good agreement. In the present study, the spin–orbit Hamiltonian contains only four elements; therefore, together with the lack of dynamical correlation in the MCSCF wave functions, the discrepancy could come from the omission of higher lying states which may mix with the \(^1\)A₁ and \(^3\)B₁ states. For CH₂ to SnH₂, it is more important to consider including dynamical electron correlation, since the effect of spin–orbit coupling on geometries is much smaller than for PbH₂.

Table II shows the calculated vibrational frequencies of adiabatic singlet and triplet states. In general, the triplet states have smaller bending frequencies than the corresponding singlet states, since the triplet bond angles are larger, and the triplet bend potentials are flatter. The stretching frequencies are larger in the triplet, due to the shorter triplet bond...
The values are calculated from the MCSCF (Møller–Plesset perturbation theory of second order) method. The singlet and triplet surfaces can be coupled through spin–orbit coupling. The nonzero matrix element that contributes to the spin–orbit coupling in a $C_{2v}$ molecule is the term arising from the $y$ component of the orbital spin angular momentum operators, respectively (see Appendix for explanation),

$$2^{-1} \alpha^2 \langle A_1 | l_y | B_1 \rangle \langle 1 | s_y | 3 \rangle,$$

where $\alpha$ is the fine structure constant, and $|1\rangle$ and $|3\rangle$ denote singlet and triplet spin functions, respectively. The choice of axes here is such that the atoms in $XH_2$ are on the $X-Z$ plane in Cartesian space. The rest of the matrix elements are zero in $C_{2v}$ symmetry. The Hamiltonian matrix for mixing these singlet and triplet substates should have the form

$$
\begin{pmatrix}
0,0 & |1,1\rangle & |1,0\rangle & |1, -1\rangle \\
|0,0\rangle & x & 0 & x \\
|1,1\rangle & 0 & 3E - \epsilon & 0 \\
|1,0\rangle & 0 & 0 & 3E - \epsilon \\
|1, -1\rangle & x & 0 & 3E - \epsilon
\end{pmatrix},
$$

(4)
triplet energies, respectively. Due to the coupling of the angular momentum quantum number $M_s$ and $\ket{S, M_s}$, where the bra and ket denote $| S, M_z \rangle$ ($S$ is the total spin angular momentum quantum number and $M_z$ is the $z$ component of the spin quantum number), $x$ denotes the nonzero matrix elements and $E_1$ and $E_3$ are the adiabatic singlet and triplet energies, respectively. Due to the coupling of the singlet and a substate of the triplet through the nonzero matrix elements, an avoided crossing between two states out of the four occurs where the adiabatic singlet and triplet states cross. The three spin functions of the triplet can be expressed as $2^{1/2}(\alpha\beta + \beta\alpha)$, $2^{1/2}(\alpha\alpha + \beta\beta)$, and $2^{1/2}(\alpha\alpha - \beta\beta)$. These transform as $A_2$, $B_1$, and $B_2$, respectively. Hence the overall symmetry of the substates of the triplet are $B_2$, $A_1$, and $A_2$, denoted as $3B_1(B_2)$, $3B_1(A_1)$, and $3B_1(A_2)$. Similarly, the singlet is denoted $1A_1(A_1)$. Mixing of two substates occurs if the overall symmetry of the two wavefunctions transform according to the same irreducible representation; here $1A_1(A_1)$ and $3B_1(A_1)$ mix, and an avoided crossing occurs. The wave functions describing the other two states, $3B_1(B_2)$ and $3B_1(A_2)$, can only couple with other high lying states with overall symmetry $B_2$ and/or $A_2$. Therefore, these two states are degenerate in the present study, and are described exclusively by triplet character. To lift these degenerate levels, requires the inclusion of higher lying states to form a larger Hamiltonian.

The singlet–triplet energy differences are compared in Table III. This table lists the energy differences for both adiabatic and relativistic singlet and triplet states. The adiabatic singlet–triplet energy gap for the heavier $XH_2$ becomes larger, except for SnH$_2$. The latter is actually smaller than that of GeH$_2$ by 1.2 kcal/mol. The relativistic singlet–triplet splitting does not differ from the adiabatic ones for CH$_2$, SiH$_2$, and GeH$_2$, since the spin–orbit coupling in these molecules is relatively small. In SnH$_2$ the relativistic singlet–triplet splitting is about 1 kcal/mol larger than the adiabatic value. On the other hand, the splitting becomes almost 6 kcal/mol larger for PbH$_2$ when the relativistic effects are introduced.

The contour maps for the relativistic $XH_2$ PES are shown in Fig. 2. Only the $1A_1(A_1)$ and $3B_1(A_1)$ states are presented here, as the middle two levels possess exclusively triplet character (vide supra) in the present study. Since there is a coupling between singlet and triplet, one side of the crossing seam on the relativistic PES is predominantly singlet character and the other side of the crossing seam possesses predominantly triplet character. This is especially clear for the species with relatively smaller spin–orbit coupling. For example, the $1A_1(A_1)$ state of CH$_2$ in Fig. 2(a)

<table>
<thead>
<tr>
<th>$XH_2$</th>
<th>Adiabatic $1A_1-3B_1$</th>
<th>Relativistic $1A_1(A_1)-3B_1(A_1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$</td>
<td>10.6</td>
<td>10.6</td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>-16.8</td>
<td>-16.8</td>
</tr>
<tr>
<td>GeH$_2$</td>
<td>-23.9</td>
<td>-24.1</td>
</tr>
<tr>
<td>SnH$_2$</td>
<td>-22.7</td>
<td>-23.7</td>
</tr>
<tr>
<td>PbH$_2$</td>
<td>-33.4</td>
<td>-39.1</td>
</tr>
</tbody>
</table>

$^a$The energy of $1A_1$ with respect to $3B_1$ in kcal/mol. A positive value indicates that the triplet is energetically more stable. The geometries of each stationary points are used for adiabatic states. For the relativistic splittings, the geometries are optimized by fitting parabolas to the calculated single point energies.

FIG. 1. Contour maps of nonrelativistic potential energy surfaces of $XH_2$ ($X=$ C, Si, Ge, Sn, Pb). The plots are $C_{2v}$ potential energy surfaces of $1A_1$ and $3B_1$ states. Successive contour lines are incremented by 0.005 hartree (1 hartree = 627.51 kcal/mol; 1 hartree = $2.195 \times 10^8$ cm$^{-1}$). The bold contours of (a) CH$_2$ indicate –6.555 and –6.570 hartree for singlet and triplet states, respectively. Similarly, (b) SiH$_2$, –4.880 and –4.855 hartree, (c) GeH$_2$, –4.855 and –4.815 hartree, (d) SnH$_2$, –4.445 and –4.410 hartree, and (e) PbH$_2$, –4.520 and –4.465 hartree. The bold lines indicate crossing seams between singlet and triplet states.

TABLE III. Singlet–triplet splittings of adiabatic and relativistic potential energies of $XH_2$.

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shows steeper contours below the crossing seam than the ones shown in Fig. 1 in which the lower part of the triplet is connected. Similarly, the $^3B_1(A_1)$ PES in Fig. 2(b) clearly shows adiabatic triplet character above the crossing seam and singlet character below the crossing seam. This becomes less apparent as X becomes heavier and the crossing seam moves to larger HXH angles.

A cross sectional view of the PES is more revealing. Figure 3 shows the cross section of the PES of CH$_2$ at a fixed bond distance 1.15 Å and the PES of PbH$_2$ at a fixed bond distance 1.885 Å. Following the top curve denoted with the squares from smaller to larger angle, the curve dramatically changes its character from triplet to singlet. The leading configurations of the wavefunction at a 90° bond angle on the upper curve have triplet character $^{2}\alpha\alpha^{1/2}[\alpha\alpha+\beta\beta]$ combination, accounting for 84.6% of the wave function. The lower curve consists of 90.8% singlet character $^{2}\alpha\beta^{1/2}[\alpha\beta+\beta\alpha]$. At 110° the upper curve consists of 90.8% singlet character, and the lower curve contains 83.5% triplet character.

Figure 3 also shows spin–orbit coupling matrix elements along the bending coordinates. The spin–orbit coupling for CH$_2$ becomes larger as angles become larger, and it reaches its maximum value at 135°. Then, it gradually decreases until 140°, then sharply decreases to zero at 180° due to symmetry (see Appendix for more explanation). The spin–orbit coupling trend in PbH$_2$ is similar to that of CH$_2$, but the maximum occurs at a smaller angle (80°) and gradually decreases to 175°, then drops steeply to zero at 180°.

**FIG. 2.** Contour maps of relativistic potential energy surfaces of XH$_2$ (X= C, Si, Ge, Sn, Pb). The plots are $C_{2v}$ potential energy surfaces of $^1A_1(A_1)$ and $^3B_1(A_1)$ states. Successive contour lines are incremented by 0.005 hartree (1 hartree=627.51 kcal/mol; 1 hartree=2.195×10$^5$ cm$^{-1}$). The bold contours of CH$_2$ indicate −6.555 and −6.570 hartree for singlet and triplet states, respectively. Similarly, (b) SiH$_2$, −4.880 and −4.855 hartree, (c) GeH$_2$, −4.855 and −4.815 hartree, (d) SnH$_2$, −4.445 and −4.410 hartree, and (e) PbH$_2$, −4.520 and −4.460 hartree.

**FIG. 3.** Cross sectional view of PES of CH$_2$ and PbH$_2$. The cross section of (a) relativistic PES of CH$_2$ at the bond length 1.15 Å is plotted. Also, the spin–orbit coupling matrix elements are shown. (b) PbH$_2$ PES (bond length 1.885 Å), in which both the adiabatic and relativistic curves, as well as the matrix elements are shown. Note the difference in the scale on the right vertical axis.
The minimum energy crossing occurs at 1.15 Å and 100° for CH₂, 1.5 Å and 127.9° for SiH₂, 1.56 Å and 135.7° for GeH₂, 1.65 Å and 134.5° for SnH₂, and 1.75 Å and 146.3° for PbH₂. Figure 4 shows the energetics and the spin–orbit coupling matrix elements along the crossing seam in each XH₂. As can be seen from the figure, the minimum energy crossing occurs at the bond length corresponding to the equilibrium structures on XH₂ upper states $^1A_1$ for CH₂ and $^3B_1$ for the rest, except for PbH₂, in which the crossing occurs at a bond length that is shorter than that at the stationary point (1.812 Å). The spin–orbit splitting (here we refer to spin–orbit splitting as the splitting between the singlet and triplet states at the crossing points) between $^1A_1(A_1)$ and $^3B_1(A_1)$ along the crossing seam is more or less constant. The spin–orbit couplings in CH₂ and SiH₂ are similar; the coupling is less than 0.5 kcal/mol, with that in SiH₂ slightly larger than CH₂. The splitting in GeH₂ is about 3 kcal/mol. As can be seen from the matrix elements, shown in Fig. 4, the splitting actually becomes smaller until 1.8 Å, then increases again, but the spin–orbit splitting is essentially constant. For SnH₂, the splitting is 6.7–5.5 kcal/mol, and the trend is similar to that found for GeH₂. The splitting for PbH₂ is 24–17 kcal/mol; again there is a decrease in splitting; then it increases.

The transition probability for intersystem crossing using a simple one dimensional Landau–Zener model was calculated for kinetic energies ranging from 0 to 2.0 eV. Figure 5 shows the transition probabilities calculated at the minimum energy crossing points for XH₂ species. A probability of unity means that the transition would take place as the molecule traverses the crossing point in one pass. As can be seen
from the figure, CH₂ and SiH₂ have a similar transition profile, in which the transition would take place only in a small kinetic energy region. On the other hand, transition is accessible at any kinetic energy in SnH₂ and PbH₂. Strong spin–orbit coupling for a given kinetic energy and a larger mass in SnH₂ and PbH₂ for given kinetic energy both contribute to larger intersystem crossing probability. GeH₂ is an intermediate case for which the transition is accessible in a range of kinetic energies.

The bending frequency of ^3B₁ CH₂ (1139.2 cm⁻¹) roughly corresponds to 0.07 eV. This translates to a transition probability 0.03. Hence, even in the small spin–orbit coupling limit and large bending frequency limit, as in CH₂, a molecule that crosses the intersection in a single pass, would have a 3% intersystem crossing probability.

CONCLUSIONS

The PES of adiabatic and spin–orbit coupled states of XH₂ (X=C, Si, Ge, Sn, and Pb) species have been compared. The geometries of SiH₂ and GeH₂ at the stationary points on the relativistic PES do not differ from the ones on the adiabatic PES due to small spin–orbit coupling. For CH₂, the singlet–triplet crossing seam lies at the position of the singlet minimum; therefore a small change in geometry is observed. The triplet state of SnH₂ is shifted 0.004 Å in bond length and 1.6° in bond angle on the relativistic PES. Due to strong spin–orbit coupling, the geometries of PbH₂ are shifted 0.005 Å and 1° for singlet and 0.015 Å and 3.4° for triplet.

Due to the coupling of singlet and triplet, the relativistic PES appears as predominantly singlet on one side and predominantly triplet on the other side of the crossing seam. If the coupling is strong, as found in PbH₂, the relativistic PES can differ dramatically from the adiabatic PES.

The spin–orbit coupling affects the singlet–triplet splitting only for SnH₂ (by 1 kcal/mol) and 6 kcal/mol for PbH₂. The splittings in CH₂, SiH₂, and GeH₂ are not affected.

The bond length at which the minimum energy crossing occurs is closer to that of the higher of the two energy states (singlet for CH₂ and triplet for the rest). The energy separation between the spin–orbit coupled states is less than 1 kcal/mol for CH₂ and SiH₂, and for GeH₂ it is about 3 kcal/mol. For SnH₂, the energy separation is 5.5–6.7 kcal/mol, and for PbH₂ it is 17–24 kcal/mol.

Transition probabilities for intersystem crossing are calculated using the Landau–Zener model. The intersystem crossing occurs only for relatively small kinetic energy regions in CH₂ and SiH₂. However, for SnH₂ and PbH₂ a transition is readily accessible at any kinetic energy due to the strong spin–orbit coupling and larger mass. GeH₂ is an intermediate case, for which the transition is accessible in a range of kinetic energies.

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APPENDIX

The spin–orbit matrix element between ^1A₁ and ^3B₁ states in C₂v symmetry can be expressed as

\[ \langle \mathrm{CT} \rangle \]
\[ \langle 1A_1 | H_{SO} | 3B_1 \rangle = \langle 1A_1 | l \cdot s | 3B_1 \rangle. \tag{A1} \]

It is assumed that both sides of Eq. (A1) are multiplied by \( \alpha^2 / 2 \) where \( \alpha \) is the fine structure constant, \( \epsilon h \alpha^2 / mc^2 \). By utilizing ladder operators, \( l \cdot s \) can be written as

\[ l \cdot s = l_z s_z + \frac{1}{2} l^+ s^- + \frac{1}{2} l^- s^+, \tag{A2} \]

where \( l_z \) is the \( z \)-component of the orbital angular momentum operator and \( s_z \) is the \( z \)-component of the spin angular momentum operator. \( l^+ \) and \( l^- \) are the raising and lowering operators for orbital angular momentum, respectively, and are defined as

\[ l^+ = l_x + il_y, \tag{A3} \]
\[ l^- = l_x - il_y. \]

Similarly, \( s^+ \) and \( s^- \) are the raising and lowering spin angular momentum operators, respectively,

\[ s^+ = s_x + is_y, \tag{A4} \]
\[ s^- = s_x - is_y. \]

Substituting Eq. (A2) into Eq. (A1) gives

\[ \langle 1A_1 | l \cdot s | 3B_1 \rangle = \langle 1A_1 | l_z B_1 \rangle \langle 1 | s_z | 3 \rangle + \frac{1}{2} \langle 1A_1 | l^+ B_1 \rangle \langle 1 | s^- | 3 \rangle \]
\[ \times \langle 1 | s^+ | 3 \rangle + \frac{1}{2} \langle 1A_1 | l^- B_1 \rangle \langle 1 | s^- | 3 \rangle \|

\[ \langle 1A_1 | l \cdot s | 3B_1 \rangle \neq 0 \text{ for triplet spin function} \]
\[ 2^{-1/2}(\alpha \alpha + \beta \beta). \]

The only nonzero spin–orbit matrix element between \( 1A_1 \) and \( 3B_1 \) states arises from the term containing the \( l_z \) angular momentum operator and the \( s_z \) spin operator for the \( \alpha \alpha + \beta \beta \) triplet spin functions.

Similar group theoretical arguments can be applied to deduce the matrix element connecting \( 1\Delta_g \) and \( 3\Sigma^- \) states of \( D_2 \) molecules is zero.

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