

Ab Initio Calculation of the Spin-Rotation Constant for ${}^2\Pi$ Diatomics

Test of the Van Vleck Approximation¹

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Ab initio calculations are carried out to determine γ^Π (true), the first-order contribution to the spin-rotation constant, γ^Π , for the $X {}^2\Pi$ ground states of OH, HF⁺, and HCl⁺ and their deuterated analogs. These calculations demonstrate that the contribution of this term to the experimentally determined value of γ^Π is small, as has been previously conjectured. Furthermore, it is found in the cases under study that the Van Vleck approximation to γ^Π (true) significantly overestimates its importance, and a more realistic approximation is presented.

The spin-rotation constant, γ^Π , for Π states of diatomic molecules has proved to be a quantity quite recalcitrant to direct measurement. The major problem is that γ^Π is *almost totally correlated* with A_D^Π , the centrifugal distortion correction to the spin-orbit constant, A^Π , although these interactions arise from different physical mechanisms. As a further complication, the combined effect of γ^Π and A_D^Π is often so small that its joint presence is difficult to detect except in very high-resolution studies or in studies of hydride diatomics.

Recently, values for γ^Π have been obtained for the ${}^2\Pi$ ground state of OD (1), and for HCl⁺ and DCl⁺ (2, 3) from an analysis of the $A {}^2\Sigma^+-X {}^2\Pi$ optical spectrum. In the procedure developed by Coxon (1), and applied by him to OD, and by Saenger, Zare, and Mathews (SZM) (2) to HCl⁺ and DCl⁺, the value of A_D^Π is independently obtained from RKR calculations, thus permitting the value of γ^Π to be extracted. In the procedure developed by Brown and Watson (BW) (3), and applied by them to HCl⁺ and DCl⁺, the different contributions of γ^Π and A_D^Π to the "effective A_D^Π constant" with isotopic substitution are used to permit their separation. The validity of the Coxon procedure seems to depend on how well $A(r)$ can be represented by using the data available on the variation of the spin-orbit constant A^Π with vibrational level. Provided $A(r)$ varies linearly with internuclear distance over the region about r_e , the Coxon procedure should be valid. This is expected to be the case for OD (4), but not necessarily for HCl⁺ and

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DCI⁺. The method of Brown and Watson requires that accurate isotopic data are available. This may limit its use in practice to hydride and deuteride molecules. However, where it can be applied, it is expected to yield superior estimates for A_D^Π and γ^Π . In either procedure, the values of γ^Π are found to be strikingly smaller than those estimated for the "true" (first-order) spin-rotation constant using an approximation first suggested by Van Vleck (5).

In his classic paper on Λ doubling in the spectra of diatomic molecules, Van Vleck states that γ^Π "is of the order m/μ times the factor of proportionality A^Π in the ordinary ${}^2\Pi$ splitting, m/μ being the ratio of the electronic mass to the reduced mass of the nuclei." SZM show that the Van Vleck approximation may be written as

$$\gamma^\Pi(\text{true}) \approx -\frac{1}{2}(m/\mu)A^\Pi, \quad (1)$$

by comparing the form of the nuclear part of the microscopic spin-other-orbit Hamiltonian to the nuclear part of the spin-orbit Hamiltonian. Equation (1) yields the estimate $\gamma^\Pi(\text{true}) \approx 0.02 \text{ cm}^{-1}$ for the $X \ {}^2\Pi$ state of OD and $\gamma^\Pi(\text{true}) \approx 0.18 \text{ cm}^{-1}$ for the $X \ {}^2\Pi$ state of HCl⁺. The experimentally derived values of the spin-rotation constant are $\gamma^\Pi = 0.00164(47) \text{ cm}^{-1}$ for OD and $\gamma^\Pi = 0.041(3) \text{ cm}^{-1}$ for the $v = 0$ level of HCl⁺ from SZM, and $\gamma_e^\Pi = 0.0091(38) \text{ cm}^{-1}$ for the equilibrium value of γ^Π in HCl⁺ from BW. In all cases, the estimate of $\gamma^\Pi(\text{true})$ based on what has become known as the Van Vleck approximation for the spin-rotation constant is *significantly larger* than the experimentally derived values of γ^Π . This has motivated us to undertake an ab initio calculation of $\gamma^\Pi(\text{true})$ so that it can be compared to the Van Vleck approximation and to the experimentally derived values.

As discussed by BW, which revises the earlier treatment of Veseth (6), the microscopic spin-rotation Hamiltonian may be written as

$$H_{sr} = \mathbf{N} \cdot \sum_i \eta(i) \mathbf{s}_i, \quad (2)$$

where \mathbf{N} is the rotational angular momentum of the nuclei and \mathbf{s}_i is the spin of the i th electron. In Eq. (2) the one-electron operator is given by

$$\eta(i) = -\frac{ge^2\hbar}{2mc^2I} \sum_K Z_K \frac{(\mathbf{r}_i - \mathbf{R}_K) \cdot \mathbf{R}_K}{|\mathbf{r}_i - \mathbf{R}_K|^3}, \quad (3)$$

where e , m , and g are the charge, mass, and g value of the electron; \hbar is Planck's constant; c is the velocity of light; and I is the moment of inertia of the nuclei. In Eq. (3) the summation is over the nuclei K . Figure 1 shows that coordinate frame where the origin is taken to be the center of mass of the molecule, and the z axis is chosen to coincide with the internuclear axis. Here \mathbf{R}_K and \mathbf{r}_i are the position vectors of the K th nucleus and i th electron, respectively, and $Z_K e$ is the charge of the K th nucleus. In the coordinate system of Fig. 1, the expectation value of η over the electronic wavefunction of the ground state and averaged over the nuclear motion for the vibrational level v becomes

$$\langle \eta \rangle_v = -\frac{ge^2\hbar}{2mc^2\langle I \rangle_v} \sum_K Z_K \left\langle \frac{R_K \cos\theta_{iK}}{r_{iK}^2} \right\rangle. \quad (4)$$

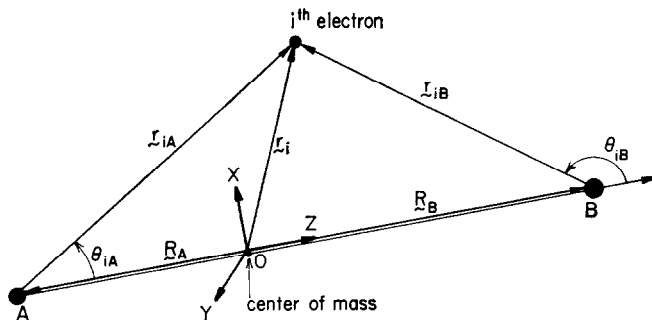


FIG. 1. Molecular coordinate system.

The electronic matrix elements are evaluated as the difference between spin-up and spin-down electrons which, for a single-determinant, restricted Hartree-Fock wavefunction, implies that the matrix elements are computed only over the unpaired π orbital. By comparing the phenomenological spin-rotation Hamiltonian $H_{sr} = \gamma \mathbf{N} \cdot \mathbf{S}$ to the microscopic one, and by relating $\langle I \rangle_v^{-1}$ to the rotational constant B_v , we finally obtain the expression

$$\gamma_v^\Pi = -1.05 \times 10^{-4} B_v^\Pi \langle \xi(R) \rangle_v, \quad (5)$$

where γ_v^Π and B_v^Π are in cm^{-1} and the quantity

$$\xi(R) = \sum_K Z_K R_K \langle \cos \theta_{iK} / r_{iK}^2 \rangle \quad (6)$$

is in atomic units (bohr^{-1}).

Ab initio calculations of γ_v^Π have been carried out for the $X^2\Pi$ ground states of OH, HCl^+ , and HF^+ (and their deuterated analogs). Wavefunctions were obtained within the restricted Hartree-Fock approximation. Calculations of similar spin hyperfine matrix elements imply that electron correlation is not very important for these properties.

For OD, calculations were done at several internuclear distances around the experimental $R_e = 1.8342a_0$ using the expansion basis set of Cade and Huo (7). Results are presented in Table I. The adequacy of the basis set was checked (at R_e) by including a number of additional functions, but this did not significantly change any of the matrix elements. It is seen that $\xi(R)$ has only a weak dependence on internuclear distance, implying that $\gamma_e^\Pi(\text{true})$ varies slowly for the lowest vibrational levels. The computed value of the spin-rotation constant for the $X^2\Pi$ state of OD at R_e is

$$\gamma_e^\Pi(\text{true}) = 3.9 \times 10^{-4} \text{ cm}^{-1}. \quad (7)$$

This is some 50 times *smaller* than the corresponding value obtained from the Van Vleck approximation. This value is also about 4 times smaller than the value of γ^Π deduced by Coxon, suggesting that the value of γ^Π derived from the experimental data does not represent the true (first-order) spin-rotation constant.

Hartree-Fock calculations were also performed for HCl^+ using the basis set of Cade and Huo (7), since tests with larger basis sets implied that it was adequate for the

TABLE I.
Electronic Matrix Elements $\xi_K(R) = Z_K R_K \langle \cos \theta_{iK} / r_{iK}^2 \rangle$ as a Function of
Internuclear Distance. All values are in atomic units
(1 bohr = 0.52918×10^{-8} cm).

<u>OD X $^2\Pi$</u>					
R	1.6342	1.7342	1.8342	1.9342	2.0342
$\xi_O(R)$	-0.03754	-0.03718	-0.03657	-0.03576	-0.03481
$\xi_D(R)$	-0.34674	-0.34208	-0.33661	-0.33055	-0.32406
$\xi(R)$	-0.38428	-0.37926	-0.37318	-0.36631	-0.35887
<u>HCl$^+$ X $^2\Pi$</u>					
R	2.2856		2.4856		2.6856
$\xi_{Cl}(R)$	-0.01109		-0.01037		-0.01016
$\xi_H(R)$	-0.27539		-0.27063		-0.26447
$\xi(R)$	-0.28648		-0.28100		-0.27463
<u>DCI$^+$ X $^2\Pi$</u>			<u>HF$^+$ X $^2\Pi$</u>		
R	2.4856		R	1.98	
$\xi_{Cl}(R)$	-0.02019		$\xi_F(R)$	-0.02004	
$\xi_D(R)$	-0.26332		$\xi_H(R)$	-0.39343	
$\xi(R)$	-0.28351		$\xi(R)$	-0.41347	

properties of interest. Results are shown in Table I. Again, there is very little variation of $\xi(R)$ with internuclear separation. At R_e we find

$$\gamma_e^{\Pi}(\text{true}) = 2.9 \times 10^{-4} \text{ cm}^{-1} \quad (8)$$

for HCl $^+$ and

$$\gamma_e^{\Pi}(\text{true}) = 1.5 \times 10^{-4} \text{ cm}^{-1} \quad (9)$$

for DCI $^+$. Once again, these values are significantly smaller than those calculated from the Van Vleck approximation or derived from the analysis of the $A-X$ spectrum.

Using the basis set of McLean and Yoshimine (8), calculations were also done for the $X^2\Pi$ state of the HF $^+$ molecule (see Table I), which is isoelectronic with OH. At R_e we find

$$\gamma_e^{\Pi}(\text{true}) = 7.6 \times 10^{-4} \text{ cm}^{-1}. \quad (10)$$

There are presently no experimental values for γ^{Π} , but the Van Vleck approximation yields $\gamma^{\Pi}(\text{true}) \approx 0.08 \text{ cm}^{-1}$.

We conclude that the Van Vleck approximation gives a gross overestimate of the true (first-order) spin-rotation constant for $^2\Pi$ states in the cases examined. Moreover,

the spin-rotation constants found from an experimental analysis of optical spectra appear to show that pseudo-spin-rotation interactions arising from the interactions of the Π state by various operators with other Σ and Δ electronic states provide the dominant contribution to γ^{II} , a result indeed first suggested by Van Vleck (5), and most recently by BW. Because the calculation of these second-order (or higher-order) contributions are rather involved, we have not pursued this topic further here.

Finally, it is of interest to consider why the Van Vleck approximation to $\gamma^{\text{II}}(\text{true})$ is so much larger than the ab initio value. The reasoning (2) behind Eq. (1) is that the spin-orbit constant A^{II} is dominated by the expectation value of the nuclear part of the spin-orbit Hamiltonian

$$H_{\text{so}}^{(n)} = -\frac{1}{2} \sum_{i,K} \left(\frac{-e_i}{mc} \right) \mathbf{s}_i \cdot \left[\left(\frac{Z_K e}{r_{iK}^3} \right) (\mathbf{r}_i - \mathbf{R}_K) \times \frac{\mathbf{v}_i}{c} \right], \quad (11)$$

while the spin-rotation constant γ^{II} is given by the expectation value of the nuclear part of the spin-other-orbit Hamiltonian

$$H_{\text{soo}}^{(n)} = \sum_{i,K} \left(\frac{-e_i}{mc} \right) \mathbf{s}_i \cdot \left[\left(\frac{Z_K e}{r_{iN}^3} \right) (\mathbf{r}_i - \mathbf{R}_K) \times \frac{\mathbf{v}_K}{c} \right], \quad (12)$$

where \mathbf{v}_i and \mathbf{v}_K are the velocities of the i th electron and the K th nucleus, respectively. Comparing $H_{\text{so}}^{(n)}$ to $H_{\text{soo}}^{(n)}$ we see that they differ formally by the replacement of \mathbf{v}_i by $-2\mathbf{v}_K$. The Van Vleck approximation simply arises by assuming that the velocities of each particle are inversely proportional to their masses.

On more careful examination of the expectation values of Eqs. (11) and (12) it is seen that additional geometrical factors enter into this comparison. For the hydride diatomics the arguments are particularly simple. The center of mass as well as the unpaired π electron may be taken, to good approximation, to be located on the heavier nucleus. Then the contribution to A^{II} is primarily from the heavier nucleus because of the factor Z_K/r_{iK}^3 averaged over the unpaired electron. On the other hand, the contribution to γ^{II} comes almost exclusively from the hydride (deuteride) nucleus (see Table I), since v_K nearly vanishes for the heavier nucleus. Hence we see that the evaluation of $\langle H_{\text{so}}^{(n)} \rangle$ and $\langle H_{\text{soo}}^{(n)} \rangle$ involve different spatial weightings. This suggests to us that for hydride (deuteride) diatomics, AH (AD), a better approximation for $\gamma^{\text{II}}(\text{true})$ would be the relation

$$\gamma^{\text{II}}(\text{true}) \approx -\frac{1}{2} A^{\text{II}} \left(\frac{m}{\mu} \right) \frac{1}{Z_A} \left(\frac{\langle r_{iA} \rangle}{R_e} \right)^3, \quad (13)$$

where $\langle r_{iA} \rangle$ is the average distance of the unpaired electron from nucleus A . One can make Eq. (13) more concrete by noting that $\langle r_{iA} \rangle$ is typically one-third to one-half the value of R_e . Thus for OD, HCl⁺, and HF⁺, $\gamma^{\text{II}}(\text{true})$ is estimated from Eq. (13) to be in the range $0.9\text{--}3.4 \times 10^{-4}$, $3.9\text{--}13 \times 10^{-4}$, and $3.3\text{--}11 \times 10^{-4} \text{ cm}^{-1}$, which should be compared with the ab initio values of 3.9×10^{-4} , 2.9×10^{-4} , and $7.6 \times 10^{-4} \text{ cm}^{-1}$, respectively.

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