Calculation of Spin-Orbit Coupling Constants in Diatomic Molecules from Hartree-Fock Wave Functions

T. E. H. Walker and W. G. Richards

Physical Chemistry Laboratory, South Parks Road, Oxford, England

(Received 13 August 1968)

Spin-orbit coupling constants are calculated from Hartree-Fock wave functions of diatomic molecules using the Dirac Hamiltonian. For first-row diatomic hydrides, agreement with experiment is good ($\sim 5\%$) provided that two-electron integrals are considered. These two-electron integrals may be interpreted as providing a shielding of the nuclear charge; they reduce the computed value of the coupling constant from that found from simple Z/r^3 terms. The applications to $^2\Pi$ states of BeH, CH, and OH are specifically considered.

The spin-orbit coupling constant A of a molecule is one of the measurable quantities that is often used by experimental spectroscopists in assigning a molecular configuration to an observed electronic state. Semiempirical[1] and approximate estimates[2] of A have been made, but we report here for the first time nearly complete *ab initio* calculations of spin-orbit coupling in some diatomic hydrides.

Although A is usually treated as a one-electron property, Blume and Watson[3,4] have shown that for atoms, an accurate value is obtained from Hartree-Fock wave functions only if the spin-other-orbit interaction between the outer electrons and the closed shells is considered. It is this interaction which provides the "shielding" of the nuclear charge.

As yet, no accurate Hartree-Fock expectation values of two-electron operators have been calculated for diatomic molecules – except, of course, for the energy and for those properties, such as the vibration frequency and equilibrium internuclear distance, that depend on the variation of the energy with internuclear distance. Calculation of the spin-orbit coupling constants of molecules is therefore of interest for two reasons: firstly, as an aid to matching up calculated configurations with observed states, and secondly, as a test of Hartree-Fock wave functions for the expectation values of two-electron operators.

The only reported nonempirical calculation of A took as the starting point the Pauli approximation to the Dirac equation

$$H_{so} = \tfrac{1}{2}\alpha^2 \sigma (\mathrm{grad}\,U) \times \vec{p} ,$$

where σ is the Pauli matrix, U is the potential, and $\vec{p}$ is the momentum of the electron. This gave a value of A for nitric oxide (NO) that was too large, which, as will be seen later, is explicable as a result of the neglect of exchange terms. Blume and Watson, in their work on atoms,[3,4] used the Dirac equation

$$H_{so} + H_{soo} = \tfrac{1}{2}\alpha^2 \sum_i (Z/r_i^3) \vec{l}_i \cdot \vec{s}_i$$
$$- \frac{\alpha^2}{2} \sum_{i \neq j} \left(\frac{\vec{r}_{ij}}{r_{ij}^3} \times \vec{p}_i \right) \cdot (\vec{s}_i + 2\vec{s}_j) ,$$

where $\vec{l}_i$ is the angular momentum of the ith electron, and $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. They showed that the spin-

other-orbit interaction between the outer electrons and the closed shells behaves as an effective one-electron operator, which is proportional to the spin-orbit coupling operator. They also gave expressions for the Hamiltonian in terms of spherical harmonics, allowing the calculation of matrix elements.

Because l is not a good quantum number in a diatomic molecule, the matrix elements between molecular orbitals cannot be given by a simple expression. However, since molecular Hartree-Fock wave functions are expanded in terms of atomic Slater-type orbitals, the molecular matrix elements can be expressed as sums of matrix elements between atomic orbitals. These matrix elements are obtained by using Blume and Watson's expressions for the Hamiltonian.

The resulting expressions contain two types of integral, the one- and two-electron integrals. The former are the simple $\langle 1/r^3 \rangle$ terms, and the latter supply the shielding which reduces the value of A from

$$\langle Z_a/r_a^3 + Z_b/r_b^3 \rangle,$$

which is the value given when only the nuclear field is considered. (Z_a and Z_b are the charges on nucleus a and b.)

Full details of these calculations will be given in a further paper.[5] The present results are calculations of A for first-row diatomic-molecule hydrides, and neglect only the very small two-electron two-centre integrals.

Table I gives the results for BeH, CH and OH. It is obvious that this method gives good values of A, while those obtained from

$$\langle Z_a/r_a^3 + Z_b/r_b^3 \rangle$$

are far too large. The two-center one-electron integrals only give a contribution of between 1 and 10% (1–2 cm^{-1}) to the final value, and this, coupled with the negligible contribution of the two-electron one-center integrals on hydrogen, makes the total neglect of the two-electron two-center integrals seem reasonable. Since they will be shielding, their inclusion would be expected to lower the value of A, and this might account for the calculated values being slightly higher than the experimental ones.

TABLE I. Calculations of molecular spin-orbit coupling constants. (i) one-center contribution, (ii) total contribution, (a) contribution from atom A, (b) contribution from hydrogen.

AH	state	Z_A/r_A^3 (i)	(ii)	Z_H/r_H^3 (i)	(ii)	shielding (a)	(b)	A (cm^{-1}) Calc	Obs[6]
BeH	$A^2\Pi_r$	5.90	5.96	0.003	0.2	−3.82	−0.001	2.34	2.14
CH	$X^2\Pi_r$	56.1	56.5	0.006	0.6	−26.8	−0.002	30.4	28
OH	$X^2\Pi_i$	216.8	217.9	0.007	0.96	−77.5	−0.006	141.4	140

TABLE II. Comparison of atomic and molecular integrals contributing to spin-orbit coupling of constants in atoms (ζ) and molecules (A).

AH	state	Z_A/r_A^3 Atom[4]	Mol	Direct Atom[4]	Mol	Exchange Atom	Mol	$\zeta_{atom} - A_{mol}$ (cm^{-1}) Calc	Exp.[4,6]
BeH	$A^2\Pi_r$	6.9	5.9	−3.0	−2.3	−1.79	−1.48	0	0.12
CH	$X^2\Pi_r$	58.5	56.1	−15.5	−15.7	−11.4	−11.4	2	4.6
OH	$X^2\Pi_i$	230	216.8	−44	−45.1	−34	−32.3	4.6	6.0

All semiempirical methods for calculating A involve the approximation that the one-center integrals remain unchanged in going from the atom to the molecule. Table II compares the atomic and molecular integrals, and the change in Z/r^3 for OH suggests that this agreement may not always hold. The Hartree-Fock wave functions reproduce the change from the atom to the molecule accurately. The exchange terms are of the same magnitude as the direct terms, underlining their importance and also suggesting the origin of the high values calculated in Ref. 2, when they were neglected.

These results show that good values of A can be obtained for hydrides, even when the two-electron two-center integrals are ignored. For diatomic molecules with nuclei of more nearly equal atomic number, this approximation may not hold, and work is continuing on such molecules.

[1]E. Ishiguro and M. Kobori, J. Phys. Soc. Japan 22, 263 (1967).

[2]J. Hellmann and C. J. Ballhausen, Theor. Chim. Acta 3, 159 (1965).

[3]M. Blume and R. E. Watson, Proc. Roy. Soc. (London) A270, 127 (1962).

[4]M. Blume and R. E. Watson, Proc. Roy. Soc. (London) A271, 565 (1963).

[5]T. E. H. Walker and W. G. Richards, to be published.

[6]G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand and Co., New York, 1950), 2nd Ed.