

Effects of the magnetic part of the Breit term on the 2Π states of diatomic hydrides

Kyoung Koo Baeck and Yoon Sup Lee

Citation: *The Journal of Chemical Physics* **100**, 2888 (1994); doi: 10.1063/1.467229

View online: <http://dx.doi.org/10.1063/1.467229>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/100/4?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

Relativistic two-component geometric approximation of the electron-positron contribution to magnetic properties in terms of Breit–Pauli spinors

J. Chem. Phys. **130**, 084102 (2009); 10.1063/1.3063639

Quantum theory of inelastic collisions of a diatomic molecule in a 2Π electronic state with an uncorrugated surface: Adoublet, spinorbit, and polarization effects in NO (X 2Π)–Ag (111) scattering

J. Chem. Phys. **80**, 3485 (1984); 10.1063/1.447105

Rotationally inelastic collisions between a diatomic molecule in a 2Π electronic state and a structureless target

J. Chem. Phys. **76**, 5974 (1982); 10.1063/1.442951

Mean dipole moment derivatives, atomic anisotropies, and effective charges of diatomic hydrides

J. Chem. Phys. **68**, 880 (1978); 10.1063/1.435823

Electromechanical Model of Diatomic Hydrides

J. Chem. Phys. **51**, 148 (1969); 10.1063/1.1671701



Effects of the magnetic part of the Breit term on the $^2\Pi$ states of diatomic hydrides

Kyoung Koo Baeck

Department of Chemistry, Kangnung National University, Kangnung 210-702, Korea

Yoon Sup Lee

Department of Chemistry and Center for Molecular Science, Korea-Advanced Institute of Science and Technology, Taejeon, 305-701, Korea

(Received 2 September 1993; accepted 3 November 1993)

All-electron relativistic self-consistent-field (RSCF) method based upon Dirac–Coulomb Hamiltonian is extended to include the magnetic part of the Breit interaction term in the SCF cycle. The explicit form of the Fock matrix for the magnetic part is derived and simplified within the restricted open-shell scheme. The effects of the magnetic part of the Breit term on spin–orbit splittings and dipole moments are investigated for $^2\Pi$ states of diatomic hydrides AH (A = Be, B, C, N, O, F, Mg, Al, Si, P, S). Calculated spin–orbit splittings are improved significantly by the inclusion of the magnetic part and approach the experimental values to within 10 cm^{-1} even for the second-row diatomic hydrides. The magnitude of the effect of the magnetic part is similar for the molecules composed of atoms in the same group regardless of the nuclear charge implying that the magnetic part and probably the whole Breit term become less important for molecules with large spin–orbit interactions. With the present RSCF method, the effects of magnetic term on properties can be estimated from expectation values. The effects of the magnetic term on dipole moments of $^2\Pi$ states of AH molecules are quite small.

I. INTRODUCTION

The Dirac–Fock (DF) theory is usually accepted as the proper starting point for all-electron relativistic calculations for atoms and molecules.^{1–4} The pure instantaneous Coulomb potential between electrons in the Dirac–Coulomb (DC) Hamiltonian, however, does not contain any relativistic corrections for two electron interactions. In order to correct for this deficiency, the Coulomb term may be complemented by the Breit term as a reasonable first approximation to more complicated and unwieldy expressions from the quantum electrodynamics.⁵ Relativistic calculations for atomic systems indicate that the Breit term constitutes an important portion of the spin–orbit interactions for light atoms and could be the source of large correlation energy for core electrons of heavy atoms.^{1,6} Since the relativistic effects for chemical properties are expected to be significant only when a molecule contains heavy atoms, the effect of the Breit term on molecular properties is usually omitted or treated as the perturbation embedded in the two-electron part of the spin–orbit coupling operators⁷ in a variety of nonrelativistic approximations.⁸ When the spin–orbit coupling is small, such approximation methods usually produce satisfactory results. For systems where the spin–orbit coupling is large, however, the nonrelativistic approximation may produce unacceptable results. The relativistic calculation is a better approach for such systems.

Our previous result⁹ for the spin–orbit splittings in diatomic hydrides with the DF theory implies that the effect of the Breit term is noticeable for molecules containing light atoms. Although there have been a few attempts^{10–13} to include the magnetic part of the Breit term in relativistic calculations for molecules, no actual calculations on spin–orbit splittings have been reported to the best of our knowl-

edge. In efforts to obtain some understanding about the role of the Breit term in spin–orbit interactions, we extend the Dirac–Fock–Roothaan method, which we refer to as the relativistic self-consistent-field (RSCF) method,^{9,14} to include the magnetic part of the Breit term in the self-consistent-field (SCF) iterations. Section II describes the theory and computational method. In the following sections, the method is applied to investigate the effect of the Breit term on spin–orbit splittings and dipole moments of the first- and second-row diatomic hydrides.

II. THEORY AND COMPUTATIONAL METHOD

The Breit interaction consists of the two parts,^{5,15} the magnetic term, H_M , and the retardation term, H_R .

$$H_B = H_M + H_R$$

$$= - \sum_{i < j} \frac{\alpha_i \cdot \alpha_j}{r_{ij}} + \sum_{i < j} \frac{[(\alpha_i \cdot \nabla_i)(\alpha_j \cdot \nabla_j)r_{ij}]}{2}. \quad (1)$$

It was demonstrated by Rosicky¹¹ that the magnetic part can be calculated with integrals usually used in Dirac–Fock calculations, but the retardation part requires additional integrals containing $(1/r_{ij}^3)$ terms. Furthermore, the inclusion of the retardation term in SCF cycle and energy optimization may cause the energy collapse due to the $(1/r_{ij}^3)$ dependence, but the magnetic term may be included in SCF cycles without such difficulties.¹⁶ Furthermore, the magnetic part accounts for the major portion of the Breit interaction. The effects of the Breit term on molecular properties or wave functions are mainly determined by the magnetic part. Therefore, only the magnetic part is explicitly treated in this work and the effect of the retardation part is estimated from the results of atomic cases.

When the four-component molecular spinors are expanded using the basis set and the resulting Dirac-Fock-Roothaan equation is derived for the RSCF method,^{9,14} the magnetic term can be added to the Fock matrix. Equivalence of the $m_w > 0$ and the $m_w < 0$ spinors for a Kramers pair yields the following equation for a closed-shell linear molecule¹⁴

$$FC = \epsilon SC, \quad (2)$$

$$F = h + \sum_{i=1}^{n_c} (2J_i - K_i^+ - K_i^- + 2D_i + X_i^+ + X_i^-), \quad (3)$$

where matrix elements of the magnetic term are expressed as the sum of the direct matrix, D , and exchange matrices, X^+ and X^- . The sum of the direct matrix elements over a closed shell vanishes as was shown by Kim.¹⁵ When the restricted open-shell scheme is used for open-shell systems where the symmetries of open shells all differ,¹⁷ only the direct matrix elements between open shells remain. As a result, two pseudoeigenvalue equations become,

$$F_c C_c = \epsilon_c S C_c, \quad (4)$$

$$F_o C_o = \epsilon_o S C_o, \quad (5)$$

where the closed-shell and the open-shell Dirac-Fock operators, F_c and F_o , respectively, are

$$F_c = H_c - S D_o F_a - F_a D_o S, \quad (6)$$

$$F_o = H_o - 2S D_c F_a - 2F_a D_c S, \quad (7)$$

$$F_a = H_o - H_c, \quad (8)$$

where the H_c for closed shells is

$$H_c = h + \sum_{i=1}^{n_c} (2J_i - K_i^+ - K_i^- + X_i^+ + X_i^-) + \frac{1}{2} \sum_{j=1}^{n_o} (2J_j - K_j^+ - K_j^- + X_j^+ + X_j^-), \quad (9)$$

and the H_{ok} for the k th open shell is

$$H_{ok} = h + \sum_{i=1}^{n_c} (2J_i - K_i^+ - K_i^- + X_i^+ + X_i^-) + \sum_{k \neq j=1}^{n_o} [J_j - K_j^+ \delta_{sk,sj} - K_j^- (1 - \delta_{sk,sj}) + D_j + X_j^+ \delta_{sk,sj} + X_j^- (1 - \delta_{sk,sj})]. \quad (10)$$

When m_w of the k th open shell and that of the j th open shell have the same sign, $\delta_{sk,sj}$ is a unity but becomes zero in other cases.

The explicit forms of a 4×4 supermatrices consisting of $n \times n$ submatrices for the direct matrix, D , and exchange matrices, X^+ and X^- , for the restricted open-shell scheme can be expressed as

$$D = \begin{pmatrix} 0 & 0 & -J^{13} + J^{24} & -2(J^{14} + J^{32}) \\ & & -J^{31} + J^{42} & \\ 0 & 0 & -2(J^{23} + J^{41}) & J^{13} - J^{24} \\ & & & +J^{31} - J^{42} \\ -J^{13} + J^{24} & -2(J^{32} + J^{14}) & 0 & 0 \\ -J^{31} + J^{42} & & & \\ -2(J^{41} + J^{23}) & J^{13} - J^{24} & 0 & 0 \\ & +J^{31} - J^{42} & & \end{pmatrix}, \quad (11)$$

$$X^+ = \begin{pmatrix} K^{33} + 2K^{44} & -K^{34} & K^{31} + 2K^{42} & -K^{32} \\ -K^{43} & 2K^{33} + K^{44} & -K^{41} & 2K^{31} + K^{42} \\ K^{13} + 2K^{24} & -K^{14} & K^{11} + 2K^{22} & -K^{12} \\ -K^{23} & 2K^{13} + K^{24} & -K^{21} & 2K^{11} + K^{22} \end{pmatrix}, \quad (12)$$

$$X^- = \begin{pmatrix} 2K^{33} + K^{44} & K^{43} & -2K^{31} - K^{42} & -K^{41} \\ K^{34} & K^{33} + 2K^{44} & -K^{32} & -K^{31} - 2K^{42} \\ -2K^{13} - K^{24} & -K^{23} & 2K^{11} + K^{22} & K^{21} \\ -K^{14} & -K^{13} - 2K^{24} & K^{12} & K^{11} + 2K^{22} \end{pmatrix}, \quad (13)$$

where the superscript i refers to the i th component of the four components. The supermatrices X^+ and X^- are not symmetric because of the imaginary nature of the small-component space. Due to the following relationships between submatrices:

$$J_{ij}^{kl} = -J_{ij}^{lk}, \quad \text{when } j, l = 1, 2, \quad i, k = 3, 4, \quad \text{or vice versa}, \quad (14)$$

$$K_{ij}^{kl} = K_{ij}^{lk}, \quad \text{when } i, j = 1, 2, \quad k, l = 3, 4, \quad \text{or vice versa}, \quad (15)$$

$$K_{ij}^{kl} = -K_{ij}^{lk}, \text{ when } j, k = 1, 2, \quad i, l = 3, 4, \text{ or vice versa,} \quad (16)$$

the above supermatrices could be simplified as

$$D = \begin{pmatrix} 0 & 0 & 2(J^{32} - J^{41}) \\ 0 & 0 & 2(J^{41} - J^{32}) \\ 2(J^{32} - J^{41}) & 0 & 0 \\ 2(J^{41} - J^{32}) & 0 & 0 \end{pmatrix}, \quad (17)$$

$$X^+ = \begin{pmatrix} K^{33} + 2K^{44} & K^{43} & K^{31} + 2K^{42} & -K^{32} \\ -K^{43} & 2K^{33} + K^{44} & -K^{41} & 2K^{31} + K^{42} \\ -K^{31} - 2K^{42} & K^{41} & K^{11} + 2K^{22} & K^{21} \\ K^{32} & -2K^{31} - K^{42} & -K^{21} & 2K^{11} + K^{22} \end{pmatrix}, \quad (18)$$

$$X^- = \begin{pmatrix} 2K^{33} + K^{44} & K^{43} & -2K^{31} - K^{42} & -K^{41} \\ -K^{43} & K^{33} + 2K^{44} & -K^{32} & -K^{31} - 2K^{42} \\ 2K^{31} + K^{42} & K^{32} & 2K^{11} + K^{22} & K^{21} \\ K^{41} & K^{31} + 2K^{42} & -K^{21} & K^{11} + 2K^{22} \end{pmatrix}. \quad (19)$$

The magnetic part of the Breit term requires additional submatrices such as J_{ij}^{kl} and K_{ij}^{kl} , which are not used in the conventional molecular DF calculations. In the RSCF method based on the DC Hamiltonian and Slater-type basis functions,^{9,14} we have added computational procedures of constructing density and Fock matrices to treat such additional submatrices which are necessary for the Dirac-Coulomb-magnetic (DCM) Hamiltonian. The use of the magnetic part as a relativistic correction to two-electron interactions was first suggested by Gaunt.¹⁸ And the magnetic part is sometimes called as the Gaunt interaction.⁴

In the present RSCF scheme, the contribution of the magnetic part of the Breit interaction can also be treated by the perturbational theory using the RSCF solutions of the DC Hamiltonian as the zeroth order. After the SCF iterations without the magnetic term converge, the contribution of the magnetic part is then calculated by the perturbation method with the final vector expansion coefficients. This is the first order perturbation calculation of the magnetic contribution. When the variational result is desired for the magnetic contribution, new SCF iterations, which include the magnetic term in the Fock matrix, start with the converged vector coefficients from the RSCF calculations with the DC Hamiltonian. Convergences for the DCM Hamiltonian are usually achieved within several additional iteration cycles.

When the speed of light is set as 10^5 a.u. to perform nonrelativistic limit calculations using the present RSCF method, there is no change in the total energy by the inclusion of the magnetic part within ten significant figures for all cases. When the true value of 137.036 a.u. for the speed of light is used, the results from the perturbational treatment of the magnetic part and those from the variational one differ by numbers below the seventh significant figure. Perturbation calculations for the magnetic part and probably the whole Breit term are reasonable for the first-

row and the second-row diatomic hydrides which are considered here. We have performed, however, variational calculations for all molecules since we are also interested in the effects of the magnetic term on wave functions and molecular properties such as the dipole moment.

III. BASIS SETS AND ATOMIC CALCULATIONS

In order to study the basis set dependence of the effect of the magnetic part of the Breit term, the total energies for Be, Ne, Mg, and Ar atoms have been calculated by the present RSCF method with and without the magnetic part of the Breit term employing various basis sets, and the results are summarized in Table I. In Table I and all other following tables, Method I refers to the RSCF calculation without the magnetic part, i.e., DC Hamiltonian, and Method II to that with the magnetic part, i.e., DCM Hamiltonian. The difference between Method I and II, which is denoted as Δ in the tables, represents the effects of the magnetic part of the Breit term on the quantity being under consideration.

Minimal-zeta (MZ) and double-zeta (DZ) basis sets used in the present calculations are from Clementi and Roettie.¹⁹ Exponents for the constrained-double-zeta (CDZ) and constrained-triple-zeta (CTZ, CTZ3) basis sets are given elsewhere.^{9,20} The constrained-quartet-zeta (CQZ) basis sets for the second-row atoms are generated by adding one tight $3p$, and one diffuse $3p$ basis function to CDZ basis sets and are listed in Table II. The constrained-quartet-zeta plus polarization (CQZP) basis sets are obtained by adding one $3d$ function to the CQZ basis sets. The triple-zeta (TZ) basis sets are constructed by adding one tight $1s$, one tight $2p$, and one diffuse $3p$ basis function to the DZ basis sets. Only the large component basis functions are discussed here for the sake of simplicity, but the actual basis sets for the present RSCF calculations always contain the small component basis functions derived from

TABLE I. Total energies of Be, Ne, Mg, and Ar atoms calculated by the RSCF method without (I) and with (II)^a the magnetic part of the Breit term using basis sets of different sizes. Energies from the numerical Dirac-Fock (DF) calculations are given for comparison. All values are in atomic units.

Atom	Basis set	I	II	Δ^b
Be	MZ	-14.559 388	-14.558 680	0.000 709
	CDZ	-14.575 254	-14.574 548	0.000 706
	CTZ	-14.575 890	-14.575 184	0.000 706
	DF	-14.575 892	-14.575 186	0.000 706
Ne	MZ	-127.949 236	-127.932 702	0.016 534
	CDZ	-128.650 993	-128.633 559	0.017 434
	CTZ	-128.689 728	-128.672 191	0.017 537
	CTZ3	-128.691 658	-128.674 114	0.017 544
Mg	DF	-128.691 976	-128.674 434	0.017 542
	MZ	-199.163 046	-199.130 883	0.032 163
	CDZ	-199.923 524	-199.889 696	0.033 828
	DZ	-199.926 733	-199.892 896	0.033 837
Ar	CQZ	-199.926 090	-199.892 244	0.033 846
	TZ	-199.934 999	-199.901 122	0.033 876
	DF	-199.935 169	-199.901 285	0.033 884
	MZ	-527.560 342	-527.423 195	0.137 147
	CDZ	-528.590 605	-528.447 833	0.142 772
	DZ	-528.665 397	-528.522 021	0.143 376
	CQZ	-528.637 338	-528.494 279	0.143 059
	TZ	-528.683 155	-528.539 677	0.143 478
	DF	-528.684 491	-528.541 053	0.143 438

^aEnergy contributions from the retardation part for Be, Ne, Mg, and Ar atoms are -4×10^{-6} , -9×10^{-4} , -2.1×10^{-3} , -1.1×10^{-2} a.u., respectively.

^bEffect of the magnetic part of the Breit term defined as $\Delta = E(\text{II}) - E(\text{I})$.

all Cartesian derivatives of the large component basis functions in order to ensure kinetic balance conditions.^{9,14,20}

Numerical atomic DF²¹ calculations without the retardation part is the basis set limit for the RSCF calculations with the magnetic part. Unlike the molecular calculations presented in the following section, the effects of the magnetic term in Table I are treated by the perturbational method so that the comparison between RSCF and DF values can be made consistently. The variationally calculated effects are almost identical as was mentioned in the last section. The effects of the magnetic term on the total energy, Δ in Table I, converge to the basis set limit faster than the total energy as the size of the basis set increases. The basis sets of the double-zeta quality are sufficient to

TABLE II. Exponents of the constrained-quartet-zeta (CQZ) basis sets for the second row atoms.

Atoms	(1s) ^a	1s	1s,2s,2p, 3s,3p	2s,2p, 3s,3p	3s,3p (3d) ^a	3s,3p,
Na	34.5000	11.3821	5.5077	2.8618	0.8478	0.4239
Mg	37.5000	12.4797	6.2801	3.1375	1.0900	0.5450
Al	40.5000	13.4923	6.8766	3.3191	1.2398	0.6199
Si	43.5000	14.4900	7.3785	3.5229	1.4142	0.7071
P	46.5000	15.4957	7.8798	3.7719	1.5968	0.7984
S	49.5000	16.4670	8.2332	3.9146	1.7384	0.8692
Cl	52.5000	17.4515	8.6114	4.0844	1.8818	0.9409
Ar	55.5000	18.4448	9.0157	4.2741	2.0264	1.0132

^aThe constrained-quartet-zeta plus polarization (CQZP) basis sets are constructed by adding these functions to CQZ basis sets.

TABLE III. Spin-orbit splittings (in cm^{-1}) of B and Al atoms (2P state) calculated by the RSCF method using basis sets of various sizes and by the numerical Dirac-Fock (DF) method without (I) and with (II) the magnetic part of the Breit term.

(B atom)		MZ	CDZ	DZ	CTZ	CTZ3	DF	Expt. ^a
Basis set								
I		14.4	18.6	19.5	20.3	20.4	20.4	
II		10.6	13.7	14.4	15.1	15.2	15.2 ^b	16.1
Δ^c		3.8	4.9	5.1	5.2	5.2	5.2	
(Al atom)		MZ	CDZ	DZ	CQZ	TZ	DF	Expt.
Basis set								
I		177.6	159.6	116.4	119.0	116.5	119.3	
II		168.1	149.9	106.3	111.9	109.4	112.2 ^b	111.9
Δ^c		9.5	9.7	10.1	7.1	7.1	7.1	

^aExperimental values taken from Ref. 8.

^bResults of the DF calculation with both the magnetic and the retardation terms are 14.6 cm^{-1} for B and 111.8 cm^{-1} for Al.

^cDifference between I and II.

reproduce the effects of the magnetic part on the total energy even though the total energy itself is not yet close to the basis set limit.

As an example of the effects of the magnetic term on open-shell atoms, RSCF calculations have been performed for the $^2P_{1/2}$ and $^2P_{3/2}$ states of the B and Al atoms with and without the magnetic term using basis sets of various sizes. The spin-orbit splittings in Table III are calculated as the difference between the total energies of $\Gamma_{1/2}(m_j=1/2)$ and $\Gamma_{3/2}(m_j=3/2)$ states. Spin-orbit splittings from the variational treatment of the magnetic part are identical to those from the perturbational treatment up to the last digits reported in the table. Results for B and Al atoms in Table III show that the effects of the magnetic term on the spin-orbit splitting are also well described by the basis sets of moderate sizes. While the TZ basis sets emphasize the inner part of a wave function, the CQZ basis sets are more flexible at the outer part. Similar to the Ar atom in Table I, the TZ basis sets are superior to the CQZ basis sets for the absolute magnitude of the magnetic term. However, the CQZ basis set is better than the TZ basis set when describing the difference of the magnetic term in two states as shown in Table III for the Al atom. Flexibility of the basis set in the valence region is important for the correct description of spin-orbit splittings of the P states while electrons in the inner shells contribute more to the absolute magnitude of the magnetic term.

The calculated spin-orbit splittings agree well with the experimental ones. The small difference between the basis set limit and experimental values is mainly caused by the omission of the retardation part and by the deficiency of the single determinant calculation. The contributions of the retardation part to the spin-orbit splittings are -0.6 and -0.4 cm^{-1} for B and Al, respectively, and are only about one-tenth of the magnetic term effects. By comparing the DF values with both magnetic and retardation terms (full Breit interaction) with experimental ones in Table III, one may conclude that electron correlations will be in the direction of increasing spin-orbit splittings, but their effects are very small for the Al atom. It appears that

TABLE IV. Electronic configurations and bond lengths, R_e 's, in atomic units used in the RSCF calculations of selected diatomic hydrides.

Molecules	State	R_e^a	Configuration
BeH	$A^2\Pi$	2.5200	$1\sim 2\sigma^2 1\pi^1$
BH ⁺	$A^2\Pi$	2.3743	$1\sim 2\sigma^2 1\pi^1$
CH	$X^2\Pi$	2.1240	$1\sim 3\sigma^2 1\pi^1$
NH ⁺	$X^2\Pi$	2.0500	$1\sim 3\sigma^2 1\pi^1$
OH	$X^2\Pi$	1.8342	$1\sim 3\sigma^2 1\pi^3$
FH ⁺	$X^2\Pi$	1.9843	$1\sim 3\sigma^2 1\pi^3$
MgH	$A^2\Pi$	3.1739	$1\sim 4\sigma^2 1\pi^4 2\pi^1$
AlH ⁺	$A^2\Pi$	3.0066	$1\sim 4\sigma^2 1\pi^4 2\pi^1$
SiH	$X^2\Pi$	2.8724	$1\sim 5\sigma^2 1\pi^4 2\pi^1$
PH ⁻	$X^2\Pi$	2.6880	$1\sim 5\sigma^2 1\pi^4 2\pi^3$
SH	$X^2\Pi$	2.5117	$1\sim 5\sigma^2 1\pi^4 2\pi^3$

^aFrom Ref. 22.

the multiconfigurational property is stronger for the $P_{1/2}$ state than for the $P_{3/2}$ state. One may expect similar trends for the contributions of the retardation and electron correlation to the spin-orbit splittings of the $^2\Pi$ states of the first- and the second-row diatomic hydrides.

IV. $^2\Pi$ STATES OF DIATOMIC HYDRIDES

Diatomic hydrides, containing the first- and the second-row atoms with the electronic state of $^2\Pi$, are selected because spin-orbit splittings and the effect of the magnetic part can be calculated by the RSCF method. RSCF calculations with DC and DCM Hamiltonians have been performed at the experimental equilibrium bond lengths²² for the electronic configurations in Table IV. In Table IV, the configurations for $^2\Pi$ states are listed, but the RSCF calculations are performed for the fine structure states composed of molecular spinors obeying the double group symmetry, i.e., $\omega\omega$ coupling for linear molecules.

One representative example for the effects of the magnetic term on the total energy, orbital energies, and the dipole moment of a molecule are given in Table V for two fine structure states of the $X^2\Pi$ state of the OH molecule at equilibrium bond length. Two states, $\Pi_{1/2}$ and $\Pi_{3/2}$, are calculated without (Method I in the table) and with (Method II) the magnetic part of the Breit term. It should be noted that resulting fine structure states in the present RSCF calculations may not be the pure Π states. States with the same Ω and different Λ can contribute in determining optimal molecular spinors for a given fine structure

state. However, we expect these mixings to be very small and will continue to label the two states as Π states. Because the magnetic term is included variationally in the SCF cycles, not only the total energy but also the orbital energies and the dipole moment are affected. Most effects of the magnetic term on the energies appear in the innermost orbitals. The spin-orbit splitting without the Breit term is -152.1 cm^{-1} and that with the magnetic term is -136.0 cm^{-1} , which is quite close to the value of -136.1 cm^{-1} obtained recently by the nonrelativistic perturbation calculation with many configurations.²³ Since the contribution of the magnetic term on the spin-orbit splitting amounts to 16.0 cm^{-1} out of the total experimental value of -139.7 cm^{-1} , the effects of the magnetic term should not be neglected in any accurate calculation of the spin-orbit splittings for the molecules of this type. The effects of the magnetic term on the dipole moment, which reflect the effects of the magnetic term on the state wave function and some other chemical properties of the molecule, are very small in magnitude as expected, but such results are not easy to confirm by other relativistic or nonrelativistic approximation methods.

RSCF values for the spin-orbit splittings of the first-row diatomic hydrides with various basis sets are given in Table VI along with the experimental values and the calculated values with the nonrelativistic perturbation method (NRPT).⁸ As expected from the results for the B and Al atoms in Table III, the values calculated with the CTZ3 basis sets seem to be within a few cm^{-1} away from the basis set limit values. An additional $3d$ basis function to the CTZ3 basis sets changes the value of spin-orbit splittings by less than 0.5 cm^{-1} . The inclusion of the magnetic term (Method II) improves the agreement between calculated and experimental values for all molecules in Table VI, and similar improvements are expected for other systems, too. The effects of the magnetic part (Δ in Table VI) increase from 1.2 cm^{-1} for BeH to 28 cm^{-1} for FH⁺ with increasing atomic number, but the relative importance of the magnetic contribution decreases with increasing atomic number.

The residual difference between the experimental and the RSCF values with the DCM Hamiltonian is mainly due to the omission of the retardation term and the correlation effects in the two fine structure states. When the retardation part is included in the atomic DF calculations with single determinants, the magnitudes of the spin-orbit

TABLE V. Total and orbital energies (in atomic units) calculated by the RSCF method without (I) and with (II) the magnetic term using the CTZ3 basis set for the $X^2\Pi$ state of OH at $R_e=1.8342\text{ a.u.}$

Method	E_{tot}	$\epsilon(1\sigma)$	$\epsilon(2\sigma)$	$\epsilon(3\sigma)$	$\epsilon(1\pi_{1/2})$	$\epsilon(1\pi_{3/2})$	\hat{d}^a
($\Pi_{1/2}$ state)							
I	-75.465 520	-20.641 53	-1.316 70	-0.658 20	-0.605 51	-0.559 39	1.837 33
II	-75.457 724	-20.636 22	-1.316 64	-0.658 17	-0.605 39	-0.559 38	1.837 08
($\Pi_{3/2}$ state)							
I	-75.466 213	-20.641 07	-1.316 57	-0.658 06	-0.560 31	-0.604 21	1.837 05
II	-75.458 344	-20.635 68	-1.316 50	-0.658 03	-0.560 18	-0.604 25	1.836 78

^aDipole moment in Debye.

TABLE VI. Spin-orbit splittings in cm^{-1} of the first-row diatomic hydrides calculated by the RSCF method without (I) and with (II) the magnetic part of the Breit interaction using basis sets of various sizes.

	Method	CDZ	DZ	CTZ	CTZ3	Expt. ^a	NRPT ^b
BeH	I	4.26	3.33	3.24	3.00		
	II	2.55	1.98	1.90	1.76	2.14	2.18
	Δ^c	1.71	1.35	1.34	1.24		
BH ⁺	I	17.3	18.3	18.7	18.5		
	II	12.6	13.4	13.8	13.6	14.0	13.8
	Δ	4.7	4.9	4.9	4.9		
CH	I	34.1	36.3	36.8	36.8		
	II	26.4	28.3	28.7	28.7	28.0	28.5
	Δ	7.7	8.0	8.1	8.1		
NH ⁺	I	98.3	100.1	102.7	102.4		
	II	80.8	82.4	84.8	84.3	77.8	78.2
	Δ	17.5	17.7	17.9	18.1		
OH	I	-142.8	-150.1	-151.9	-152.1		
	II	-127.9	-134.2	-135.8	-136.0	-139.7	-140.6
	Δ	14.9	15.9	16.1	16.1		
FH ⁺	I	-298.8	-307.3	-313.6	-313.7		
	II	-272.2	-280.0	-285.8	-285.9	-292.9	-293.3
	Δ	26.6	27.3	27.8	27.8		

^aExperiment from Ref. 22.^bNonrelativistic perturbation calculation from Ref. 8.^cAbsolute value of the difference between I and II.

splittings for the B and F atoms decrease by 0.6 and 6.1 cm^{-1} , respectively. The difference of shell structures between nonrelativistic and relativistic calculations can contribute to the calculated spin-orbit splittings of F-like atoms,²⁴ but does not seem to affect the spin-orbit splittings of the diatomic hydrides,⁹ probably due to the lower symmetry in molecules. Since the magnitudes of the best basis set (CTZ3) values for BH⁺ and FH⁺ are smaller than the experimental ones by 0.4 and 7.0 cm^{-1} , respectively, the correlation effects are estimated to be about twice in magnitude but opposite in direction compared with the effect of the retardation term under the assumption that the retardation contributions to the spin-orbit splittings are same for the atom and the corresponding molecular ion. In any case, the combined effects of the retardation and electron correlations are still considerably smaller than the effects of the magnetic term. The present method which neglects the retardation term and the correlation effects appears to be a reasonable approach to treat spin-orbit splittings in these molecules. Nonrelativistic perturbation methods are also quite successful for these molecules. The agreements with the experimental values are even better for the NRPT method as shown in Table VI. The NRPT method in Table VI considers all one- and two-electron spin-orbit operators corresponding to the complete Breit interaction and the moderate amount of electron correlations.

The results for diatomic hydrides containing the second row atoms in Table VII display the basis set dependence similar to the first row diatomic cases. The values calculated with CQZP basis sets are probably within a few cm^{-1} of the basis set limit. The magnitudes of the effects of the magnetic term on the spin-orbit splittings are computed fairly accurately by the CQZ basis sets. The magnitude of the magnetic contribution increases, but the relative importance decreases for hydrides containing atoms

with higher atomic numbers. When the results in Table VI and Table VII are compared, it can be noted that the effects of the magnetic term are almost same in magnitude for a pair of diatomic hydrides containing atoms of the same group. The magnetic term constitutes a part of the two-electron part of the spin-orbit coupling operator. While the contribution of the one-electron part increases with the nuclear charge, that of the two-electron part mainly depends on the effective nuclear charge or densities of electrons. As a result, the relative importance of the magnetic term and the whole Breit term will become less important for molecules containing heavy atoms. This tendency is especially pronounced for the differential quantities like spin-orbit splittings of the ²II state. The effects of the magnetic term on spin-orbit splittings depend on the number of valence electrons and not on the nuclear charge.

In contrast to the first-row diatomic hydrides where the nonrelativistic method produces better results for the spin-orbit splittings than the RSCF method with the DCM Hamiltonian, the NRPT values are in worse agreement with the experimental ones compared with the RSCF results for the second-row diatomic hydrides. A recent nonrelativistic calculation²³ for spin-orbit splittings of SH reports a respectable value of -385.53 cm^{-1} compared with the NRPT value of -351.6 cm^{-1} in Table VII, indicating that extensive configuration mixing is necessary for the accurate spin-orbit splittings for this molecule. On the other hand, the results of the present RSCF method seem to imply the relative unimportance of the electron correlation effect in methods utilizing the Dirac operator. The combined contributions of the retardation term and the electron correlations to the spin-orbit splittings are less than 10 cm^{-1} both for the first-row (Table VI) and the second-row diatomic hydrides (Table VII). The results in Table VII demonstrate that the NRPT methods for the

TABLE VII. Spin-orbit splittings (in cm^{-1}) of the second-row diatomic hydrides calculated by the RSCF method without (I) and with (II) the magnetic part of the Breit interactions using various basis sets.

	Method	CDZ	DZ	CQZ	CQZP	Expt. ^a	NRPT ^b
MgH	I	65.0	37.9	34.3	33.0		
	II	60.8	35.4	32.0	30.9	35.0	53.4
	Δ^c	4.2	2.5	2.3	2.1		
AlH ⁺	I	114.2	114.2	113.5	113.0		
	II	107.4	107.4	106.7	106.2	108.0	91.1
	Δ	6.8	6.8	6.8	6.8		
SiH	I	176.2	155.0	158.0	157.4		
	II	166.4	146.3	149.1	148.6	142.0	126.8
	Δ	9.8	8.7	8.9	8.8		
PH ⁻	I	-248.2	-205.9	-195.7	-195.2		
	II	-236.3	-195.7	-186.1	-185.7		-173.1
	Δ	11.9	10.2	9.6	9.5		
SH	I	-407.0	-397.5	-401.2	-400.4		
	II	-388.9	-379.7	-383.2	-382.4	-382.4	-351.6
	Δ	18.1	17.8	18.0	18.0		

^aExperiment from Ref. 22.^bNonrelativistic perturbation calculation from Ref. 8.^cDifference between I and II.

spin-orbit coupling become more cumbersome while the relativistic approaches such as the present RSCF method maintain the same level of accuracy when spin-orbit coupling is large.

The effects of the magnetic term on the distribution of the valence electrons in a molecule may be estimated from those on the dipole moments. The dipole moments calculated with the basis sets CTZ3P for the first-row atoms and the CQZP for the second-row atoms are given in Table VIII. The CTZ3P basis sets are made by adding one 3d function to the CTZ3 basis sets, and the CQDZ sets are given in Table II. There are four sets of values in Table VIII. The difference in the dipole moments between two fine structure states, $\Pi_{1/2}$ and $\Pi_{3/2}$, is due to the spin-orbit coupling operator contained in the DC Hamiltonian (Method I) or in the DCM Hamiltonian (Method II). The effects of the magnetic term can be obtained by comparing I and II for each fine structure state. All four values for a given molecule are quite similar as shown in Table

VIII, indicating that the DC and/or the magnetic part of the Breit operator produces very small differential effects for two fine structure states. Differences are consistently smaller than 10^{-3} D. No attempt is made to analyze the trends exhibited by the differences in the dipole moments, mainly because the differences are too small to influence any properties of interest. The differences resulting from the magnetic term are in the same range as the differences between two fine structure states, but are similar in magnitude and direction for two states. It appears that the magnetic part affects the wave functions of two fine structure states in a similar manner for the molecular states which have been considered here.

V. CONCLUSIONS

The RSCF method for molecules is extended to include the magnetic part of the Breit term in the SCF cycle, and the effects of the Breit term on spin-orbit splittings and dipole moments have been investigated for diatomic hydrides containing the first- and second-row atoms. The calculated spin-orbit splittings are improved significantly by the inclusion of the magnetic term and approach the experimental values to within 10 cm^{-1} even for the second-row diatomic hydrides where the nonrelativistic method requires extensive multiconfigurations to produce similar results. The effects of the magnetic term on dipole moments are quite small for the molecules considered here, but the total differential effects of DC and DCM Hamiltonians on two fine structure states are also found to be quite small. This does not imply that dipole moments can be accurately calculated by the nonrelativistic method. On the contrary, the RSCF method is probably one of the simpler all-electron methods for the treatment of molecules containing heavy atoms.

The relative importance of the contributions from the magnetic term decreases when compared with those from other terms in the DCM Hamiltonian. It appears that the

TABLE VIII. Dipole moments (in Debye) of the two $^2\Pi$ fine structure states ($\Pi_{1/2}$ and $\Pi_{3/2}$) of the hydrides calculated without (I) and with (II) the magnetic part of the Breit term. Dipole moments are defined with the origin at the A atom and the H atom located at the positive direction.

(Molecule) Method	$\Pi_{1/2}$		$\Pi_{3/2}$	
	I	II	I	II
BeH	-3.0275	-3.0279	-3.0274	-3.0279
BH ⁺	-0.2030	-0.2033	-0.2029	-0.2032
CH	1.6452	1.6452	1.6453	1.6453
NH ⁺	2.6125	2.6124	2.6129	2.6126
OH	1.7120	1.7121	1.7118	1.7118
FH ⁺	3.1500	3.1492	3.1493	3.1489
MgH	-2.7141	-2.7136	-2.7085	-2.7085
AlH ⁺	-1.4606	-1.4612	-1.4584	-1.4595
SiH	0.3093	0.3091	0.3100	0.3094
PH ⁻	0.0399	0.0398	0.0395	0.0394
SH	0.9569	0.9563	0.9560	0.9555

magnetic term and probably the whole Breit interaction can be neglected for most properties of chemical interests when molecules contain heavy atoms. This is encouraging for the approximate methods which mimic the DC Hamiltonian, e.g., relativistic effective core potential methods, since the relativistic corrections to two electron interactions are not very well developed for such approximation methods and are probably very difficult to incorporate. Additional applications of the present method on nonhydrides and heavier diatomic molecules are in progress along with the extension of the RSCF method to include electron correlations.

ACKNOWLEDGMENT

This research is in part supported by Korean Science and Engineering Foundation (KOSEF 921-0300-024-1).

¹ *Atomic Theory Workshop on Relativistic and QED Effects in Heavy Atoms*, edited by H. P. Kelly and Y. K. Kim (AIP, New York, 1985).

² *Relativistic Effects in Atoms, Molecules, and Solids*, edited by G. L. Malli (Plenum, New York, 1983).

³ *Relativistic Effects in Atoms and Molecules*, edited by S. Wilson, Vol. 2, Methods in Computational Chemistry (Plenum, New York, 1988).

⁴ *The Effects of Relativity on Atoms, Molecules, and the Solid State*, edited by I. P. Grant, B. Gyorffy, and S. Wilson (Plenum, New York, 1991).

⁵ H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957).

⁶ J. Hata, I. P. Grant, and B. P. Das, *J. Phys. B* **16**, L189 (1983); **17**, L1 (1983).

⁷ S. R. Langhoff and C. W. Kern, *Applications of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), p. 381.

⁸ W. G. Richards, H. P. Trivedi, and D. L. Cooper, *Spin-Orbit Coupling in Molecules* (Clarendon, Oxford, 1981).

⁹ K. K. Baeck and Y. S. Lee, *J. Chem. Phys.* **93**, 5775 (1990); K. K. Baeck and Y. S. Lee, *Chem. Phys. Lett.* **147**, 367 (1988).

¹⁰ G. Malli and J. Oreg, *J. Chem. Phys.* **63**, 830 (1975).

¹¹ F. Rosicky, *Chem. Phys. Lett.* **85**, 195 (1982).

¹² K. G. Dyall, K. Faegri, Jr., P. R. Taylor, and H. Partridge, *J. Chem. Phys.* **95**, 2583 (1991); K. G. Dyall, *ibid.* **96**, 1210 (1992); **98**, 2191, (1993).

¹³ O. Visser, L. Visscher, P. J. C. Aerts, and W. C. Nieuwpoort, *J. Chem. Phys.* **96**, 2910 (1992).

¹⁴ Y. S. Lee and A. D. McLean, *J. Chem. Phys.* **76**, 735 (1982); A. D. McLean and Y. S. Lee, *Studies Phys. Theoret. Chem.* **21**, 219 (1982).

¹⁵ Y. K. Kim, *Phys. Rev.* **154**, 17 (1967).

¹⁶ W. Buchmuller, *Phys. Rev. A* **18**, 1784 (1978).

¹⁷ K. K. Baeck, M. S. Lee, and Y. S. Lee, *Chem. Phys. Lett.* **198**, 273 (1992).

¹⁸ J. A. Gaunt, *Proc. R. Soc. London Ser. A* **122**, 513 (1929); **124**, 163 (1929).

¹⁹ E. Clementi and C. Roetti, *Atom. Data Nucl. Data Tables*, **14**, 177 (1974).

²⁰ Y. S. Lee, K. K. Baeck, and A. D. McLean, *J. Comp. Chem.* **10**, 112 (1989).

²¹ J. P. Desclaux, *At. Data Nucl. Data Tables* **12**, 311 (1973).

²² K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950).

²³ R. D. Vivie, C. M. Marian, and S. D. Peyerimhoff, *Mol. Phys.* **63**, 3 (1988).

²⁴ K. N. Huang, Y. K. Kim, K. T. Cheng, and J. P. Desclaux, *Phys. Rev. Lett.* **48**, 1245 (1982); Y. K. Kim and K. N. Huang, *Phys. Rev. A* **26**, 1984 (1982).