



Calculation of hyperfine structure constants of small molecules using Z-vector method in the relativistic coupled-cluster framework

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Abstract. The Z-vector method in the relativistic coupled-cluster framework is employed to calculate the parallel and perpendicular components of the magnetic hyperfine structure constant of a few small alkaline earth hydrides (BeH, MgH, and CaH) and fluorides (MgF and CaF). We have compared our Z-vector results with the values calculated by the extended coupled-cluster (ECC) method reported in *Phys. Rev. A* **91** 022512 (2015). All these results are compared with the available experimental values. The Z-vector results are found to be in better agreement with the experimental values than those of the ECC values.

1. Introduction

The precise calculation of the wavefunction of a many-electron system is extremely important to obtain accurate result of different atomic and molecular properties. For the calculation of various properties like hyperfine structure (HFS) constants, and various parity (\mathcal{P}) and time reversal (\mathcal{T})-violating interaction constants (like effective electric field (E_{eff}) experienced by the unpaired electron and scalar-pseudoscalar (S-PS) \mathcal{P} , \mathcal{T} -odd interaction constant (W_s)), an accurate wavefunction is needed in the near nuclear region. The calculation of these types of \mathcal{P} , \mathcal{T} -odd properties is very important because they cannot be measured by any experimental technique and are very important to unravel many mysteries of physics.¹⁻⁷ The accuracy of these types of properties can be accessed by comparing theoretically obtained HFS constants with available experimental values. Light hetero-diatomic molecules are very useful for testing the accuracy of wavefunction in the near nuclear region as the magnetic moment of both nuclei interacts with the unpaired electron to produce HFS splitting.⁸

The accurate calculation of HFS needs to include both relativistic and electron correlation effects in an intertwined manner. The Dirac-Hartree-Fock (DHF) method is the most elegant way to include the relativistic effects in a single determinant theory. The dynamic

correlation of opposite spin electrons which is missed in DHF theory can be included by single reference coupled cluster (SRCC) method.^{9,10} The SRCC equations can be solved either by variational (VCC) or non-variational (NCC) way. In NCC, the property calculation can be done either in the expectation value or in the energy derivative method. In general, these two methods produce two different results as the NCC is non-variational and thus, does not satisfy the generalized Hellmann-Feynman (GHF) theorem.^{11,12} However, the energy derivative method is superior to the expectation value method because the first-order energy derivative is the corresponding expectation value plus some additional terms, which makes the derivative approach closer to full configuration interaction property value. The expectation value in NCC also produces a non-terminating series and one needs to use some truncation scheme for practical purpose. This introduces an additional error.

On the other hand, VCC satisfies the GHF theorem and thus, both expectation value and derivative methods produce identical results. Among many VCC,¹³ extended coupled-cluster (ECC),^{14,15} expectation value coupled-cluster (XCC),^{16,17} and unitary coupled-cluster (UCC)¹⁸⁻²³ are the most familiar in literature. Recently, we implemented ECC in four-component relativistic framework to calculate the first-order properties and we applied this to calculate the magnetic HFS constants of atoms and molecules.²⁴ In ECC, the amplitude equations for both excitation and deexcitation operators

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are coupled and thus, we have to solve them simultaneously. In the Z-vector method (an energy derivative method in NCC),^{25,26} the equations for excitation operators are decoupled from the equations of deexcitation operators. This accelerates the convergence in Z-vector method and saves enormous computational time.

In this paper, we have calculated parallel and perpendicular magnetic HFS constants of BeH, MgH, CaH, MgF, and CaF molecules using the Z-vector coupled-cluster method and compared them with the experimental results wherever available. We also compared our results with the ECC results taken from Ref.²⁴

The manuscript is organized as follows. A brief overview of the Z-vector method including concise details of parallel and perpendicular components of the magnetic HFS constant is described in Sec. 2. Computational details are given in Sec. 2.3. We presented our calculated results and discussed about those in Sec. 3 before making the final remark in Sec. 4. Atomic unit is used consistently unless stated otherwise.

2. Theory and Computational Details

2.1 Z-vector method

In a single determinant theory, the DHF method yields the best description of the ground state and for this reason, it is used as a reference state for the treatment of missing electron correlation. The Dirac-Coulomb (DC) Hamiltonian is used in this calculation and can be expressed as

$$H_{DC} = \sum_i \left[-c(\vec{\alpha} \cdot \vec{\nabla})_i + (\beta - \mathbb{1}_4)c^2 + V^{nuc}(r_i) + \sum_{j>i} \frac{1}{r_{ij}} \mathbb{1}_4 \right], \quad (1)$$

where, α and β are the usual Dirac matrices, c is the speed of light, $\mathbb{1}_4$ is the 4×4 identity matrix. $V^{nuc}(r_i)$ is the nuclear potential term and we have used Gaussian charge distribution for this purpose. The DHF method transforms the complicated many-electron problem into many one-electron problems and in this process misses the correlation between opposite spin electrons. In this work, the missing dynamic correlation is incorporated by using the SRCC method. The SRCC wavefunction is given by

$$|\Psi_{cc}\rangle = e^T |\Phi_0\rangle, \quad (2)$$

where Φ_0 is the DHF wavefunction and T is the coupled-cluster excitation operator which is given by

$$T = T_1 + T_2 + \dots + T_N = \sum_n T_n, \quad (3)$$

with

$$T_m = \frac{1}{(m!)^2} \sum_{ij\dots ab\dots} t_{ij\dots}^{ab\dots} a_a^\dagger a_b^\dagger \dots a_j a_i, \quad (4)$$

where i, j are the hole and a, b are the particle indices. $t_{ij\dots}^{ab\dots}$ are the cluster amplitudes corresponding to the cluster operator T_m . The equations for n-body cluster amplitudes are given as

$$\langle \Phi_{i\dots}^{a\dots} | (H_N e^T)_c | \Phi_0 \rangle = 0, \quad (5)$$

where H_N is the normal ordered DC Hamiltonian and subscript c means only the connected terms exist in the contraction between H_N and T . In the coupled-cluster single and double (CCSD) model, $T = T_1 + T_2$. The explicit equations for T_1 and T_2 are given as

$$\langle \Phi_i^a | (H_N e^T)_c | \Phi_0 \rangle = 0, \quad \langle \Phi_{ij}^{ab} | (H_N e^T)_c | \Phi_0 \rangle = 0. \quad (6)$$

Once the T_1 and T_2 amplitudes are solved, the correlation energy can be obtained as

$$E^{corr} = \langle \Phi_0 | (H_N e^T)_c | \Phi_0 \rangle. \quad (7)$$

The SRCC solved in this way is non-variational in nature and thus, the SRCC energy is not optimized with respect to the molecular orbital coefficients (C_M) and the determinantal coefficients (C_D) in the expansion of the correlated many-electron wavefunction for a fixed nuclear geometry.¹¹ Therefore, for the energy derivative calculation, one needs to incorporate the derivative of energy with respect to C_M and C_D in addition to the derivative of these two coefficients with respect to the external field parameter. However, the derivative terms related to C_D and C_M can be integrated by solving linear equations for each coefficient where the solutions are in general, perturbation dependent. This means, for each type of properties, one needs to solve a different set of linear equations. However, in Z-vector method, this can be avoided and the derivative terms related to C_D can be incorporated by the introduction of a perturbation independent operator, Λ .²⁶ The antisymmetrized form of the Λ operator is given as

$$\Lambda = \Lambda_1 + \Lambda_2 + \dots + \Lambda_N = \sum_n \Lambda_n, \quad (8)$$

where

$$\Lambda_m = \frac{1}{(m!)^2} \sum_{ij\dots ab\dots} \lambda_{ij\dots}^{ab\dots} a_i^\dagger a_j^\dagger \dots a_b a_a, \quad (9)$$

where i, j are the hole and a, b are the particle indices. $\lambda_{ij\dots}^{ab\dots}$ are the cluster amplitudes corresponding to the cluster operator Λ_m . From the form of the Λ operator,

Table 1. Parallel (A_{\parallel}) and perpendicular (A_{\perp}) magnetic hyperfine structure constant of molecules in MHz.

Molecule	Atom	A_{\parallel}					A_{\perp}				
		ECC	Z-vector	Expt. ³⁴	$\delta\%$		ECC	Z-vector	Expt. ³⁴	$\delta\%$	
					ECC	Z-vector				ECC	Z-vector
BeH	¹ H	204.1	199.5	201(1) ⁸	1.5	0.8	185.6	181.0	190.8(3) ⁸	2.8	5.4
	⁹ Be	-200.6	-201.3	-208(1) ⁸	3.7	3.3	-186.0	-186.8	-194.8(3) ⁸	4.7	4.3
MgH	¹ H		276.2	298(1) ³⁵		7.9		271.1	264(1) ³⁵		2.6
	²⁵ Mg		-188.1	-226(3) ³⁵		20.1		-172.0	-218(1) ³⁵		26.7
CaH	¹ H	146.4	143.7	138(1) ³⁵	5.7	4.0	141.9	139.0	134(1) ³⁵	5.6	3.6
	⁴³ Ca	-321.6	-331.2				-295.7	-305.2			
MgF	¹⁹ F	320.9	322.6	331(3) ³⁶	3.1	2.6	153.3	148.7	143(3) ³⁶	6.7	3.8
	²⁵ Mg	-282.6	-281.8				-270.4	-269.6			
CaF	¹⁹ F		131.7	149(3) ³⁶		13.1		83.8	106(3) ³⁶		26.5
	⁴³ Ca		-426.4					-408.9			

it is clear that it is a de-excitation operator. The Λ amplitude equation is given by

$$\langle \Phi_0 | [\Lambda(H_N e^T)_c] | \Phi_{i..}^{a..} \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_{i..}^{a..} \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_{int} \rangle \langle \Phi_{int} | \Lambda | \Phi_{i..}^{a..} \rangle = 0, \quad (10)$$

where Φ_{int} is the determinant corresponding to the intermediate excitation between Φ_0 and $\Phi_{i..}^{a..}$. In CCSD model, $\Lambda = \Lambda_1 + \Lambda_2$ and the explicit equations for the amplitudes of Λ_1 and Λ_2 operators are given by

$$\langle \Phi_0 | [\Lambda(H_N e^T)_c] | \Phi_i^a \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_i^a \rangle = 0, \quad (11)$$

$$\langle \Phi_0 | [\Lambda(H_N e^T)_c] | \Phi_{ij}^{ab} \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_{ij}^{ab} \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_i^a \rangle \langle \Phi_i^a | \Lambda | \Phi_{ij}^{ab} \rangle = 0. \quad (12)$$

Finally, the energy derivative can be given as

$$\Delta E' = \langle \Phi_0 | (O_N e^T)_c | \Phi_0 \rangle + \langle \Phi_0 | [\Lambda(O_N e^T)_c] | \Phi_0 \rangle, \quad (13)$$

where, O_N is the derivative of the normal ordered perturbed Hamiltonian with respect to the external field of perturbation.

2.2 Magnetic hyperfine structure constants

The interaction of the electromagnetic field generated by electrons with the magnetic dipole moment of the nucleus is responsible for the magnetic HFS.²⁷ The magnetic vector potential (\vec{A}) due to the magnetic moment ($\vec{\mu}_k$) of a nucleus is given as

$$\vec{A} = \frac{\vec{\mu}_k \times \vec{r}}{r^3}. \quad (14)$$

The perturbed HFS Hamiltonian of an atom due to \vec{A} in the Dirac theory is given by

$$H_{hyp} = \sum_i^n \vec{\alpha}_i \cdot \vec{A}_i, \quad (15)$$

where n is the total no of electrons and α_i denotes the Dirac α matrices for the i^{th} electron. For a diatomic molecule, the z (along the molecular axis) and x or y (i.e., perpendicular to molecular axis) projection of the expectation value of the corresponding perturbed HFS Hamiltonian gives the parallel (A_{\parallel}) and perpendicular (A_{\perp}) magnetic HFS constant, respectively. The expression for A_{\parallel} and A_{\perp} can be written as

$$A_{\parallel(\perp)} = \frac{\vec{\mu}_k}{I\Omega} \cdot \langle \Psi_{\Omega} | \sum_i^n \left(\frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^3} \right)_{z(x/y)} | \Psi_{\Omega(-\Omega)} \rangle, \quad (16)$$

where I is the nuclear spin quantum number and Ω represents the z component (along molecular axis) of the total angular momentum of the diatomic molecule.

2.3 Computational details

We have used the locally modified version of DIRAC10²⁸ program package to solve the DHF Hamiltonian and to construct the one-electron and two-electron integrals and the HFS integrals. Gaussian charge distribution is considered as nuclear model where the nuclear parameters²⁹ are taken as default values of DIRAC10 program package. The basis functions are represented in scalar basis and restricted kinetic balance (RKB)³⁰ condition is applied to generate the small component basis functions from the large component basis functions. The unphysical solutions are removed by diagonalizing the free particle Hamiltonian. This generates equal number of positronic and electronic orbital. In our molecular calculations, we have used aug-cc-pCV5Z³¹ for H atom and aug-cc-pCVQZ³¹ for F, Be, and Mg atoms and dyall.cv4z³² basis for Ca atom. All the generated orbitals are taken for the correlation calculation of BeH. The cutoff used for the correlation calculations of MgH, MgF, CaH, and CaF molecules

are 10 a.u., 10 a.u., 15 a.u., and 15 a.u., respectively. The bond-length used for the BeH, MgH, CaH, MgF, and CaF molecules are 1.343 Å, 1.7297 Å, 2.003 Å, 1.750 Å, and 1.976 Å, respectively.³³

3. Results and Discussion

The aim of our present study is to show that the Z-vector method can produce a very good quality wavefunction in the near nuclear region of small molecules and for this purpose we have calculated the HFS constants of some small molecules. In Table 1, we present the A_{\parallel} and A_{\perp} HFS constants of BeH, MgH, CaH, MgF, and CaF using the Z-vector method in the relativistic coupled-cluster framework. The HFS constants of BeH, MgF and CaH using the Z-vector method are also compared with the values obtained in the ECC method reported in Ref.²⁴ For this reason, we have taken the identical basis and cutoff for BeH, MgF and CaH as reported in Ref.²⁴ These values are compared with the available experimental values^{8,34–36} and the deviations are presented as $\delta\%$. From Table 1, it is clear that our Z-vector results are in close agreement with the experimental values. The highest and lowest deviations of Z-vector values of A_{\parallel} occur for ^{25}Mg of MgH and ^1H of BeH, respectively, where the deviations are 37.9 MHz and 1.5 MHz, respectively. For the Z-vector results of A_{\perp} , the highest and lowest deviations appear for ^{25}Mg of MgH and ^1H of MgH, respectively, where the deviations are 46 MHz and 7 MHz, respectively. From the above observation, we can comment that the Z-vector method can produce very good quality wavefunction in the nuclear region of small molecules. In Figures 1 and 2, we have compared the relative deviations of A_{\parallel} and A_{\perp} values, respectively, between ECC and Z-vector method. From these figures, it is clear that the Z-vector method always produces better results than the ECC

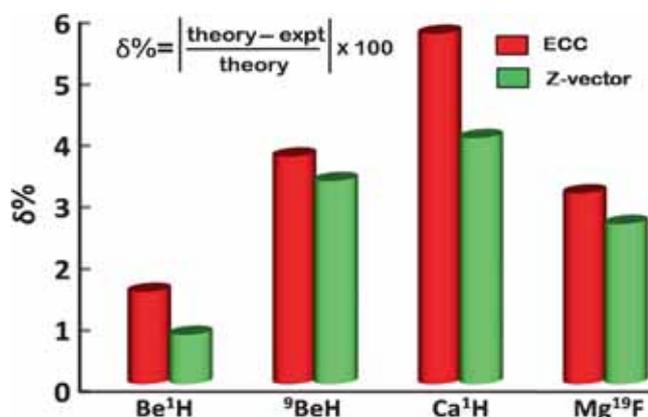


Figure 1. Comparison of relative deviations of A_{\parallel} values between ECC and Z-vector method.

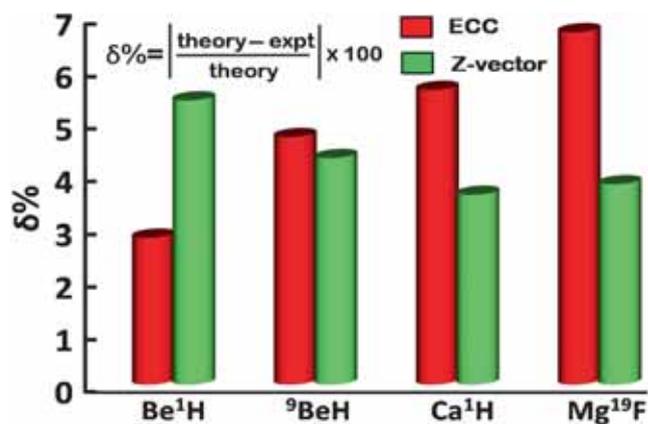


Figure 2. Comparison of relative deviations of A_{\perp} values between ECC and Z-vector method.

method. The only exception is for A_{\perp} value of ^1H in BeH where the difference between ECC and Z-vector values is only 4.6 MHz. Although the ECC functional generates a terminating series, in the CCSD approximation, the natural truncation produces some computationally very costly terms. To avoid this, the ECC functional in Ref.²⁴ is truncated in such a way that either the left vector or the right vector is linear in a double linked form. This introduces some additional errors, which may be the reason for the poor performance of the ECC method compared to the Z-vector method.

4. Conclusions

In conclusion, we have applied the Z-vector method in the relativistic coupled-cluster framework to calculate the parallel and perpendicular components of the magnetic HFS constant of small diatomic molecules. Our results show that the Z-vector can produce an accurate wavefunction in the nuclear region of small molecules. In Ref.³⁷, we have shown that the Z-vector method can produce very good wavefunction in the nuclear region of moderately heavy molecules like SrF. Similarly, Z-vector method can also produce an accurate wavefunction in the nuclear region of heavy diatomic molecules.^{38–40} So, altogether, we can say that the Z-vector is a very reliable method to produce high quality wavefunction in the core region. In this work, we have also shown that the Z-vector method can produce more accurate results for the magnetic HFS constant than the ECC method and thus, is more reliable for the calculation of various \mathcal{P} , \mathcal{T} -odd interaction constants.

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