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Relativistic theory of the magnetic shielding constant: a Dirac–Fock finite perturbation study

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Abstract

Four-component relativistic theory of the magnetic shielding constant is presented, based on the matrix Dirac–Fock finite perturbation method and implemented for numerical calculations with the MOLFDIR program. In contrast to the non-relativistic and quasi-relativistic formalisms, the shielding constant is written as a single term. Our formulation avoids explicit use of the positron states, in contrast to the conventional sum-over-states formalism. The magnetic shielding constants of the noble gas atoms, He through Xe, and those of H_2, HF and HCl are calculated and compared with values obtained in non-relativistic calculations. © 1998 Elsevier Science B.V.

1. Introduction

The importance of relativistic effects on magnetic shielding was suggested theoretically many years ago, but almost no actual calculations have been performed due to the lack of a computationally systematic method [1–4].

Recently we have presented a method for computing the magnetic shielding constant under the influence of the spin–orbit (SO) interaction using unrestricted Hartree–Fock (UHF) wavefunctions with the finite perturbation (FP) method. We call the approach the SO–UHF method [5]. This method has been applied to the proton, C [5], Ga and In [6] chemical shifts in the hydrogen and methyl halides and gallium and indium tetrahalides. Further, replacing the SO operator with an SO effective core potential [7], this method was applied to Si [8], Al [8], Sn [10], Nb and Ti [11] chemical shifts in their tetrahalides. The normal halogen dependence (NHD) of the chemical shifts of these compounds were poorly reproduced in the absence of the SO interaction and thus the importance of the SO effect was amply demonstrated.

The spin-free relativistic (SFR), i.e. mass–velocity (MV) and Darwin (DW), terms have further been incorporated into a quasi-relativistic two-component no-pair formalism using the SO–UHF method [12] and applied to H [12], Hg [13] and W [14] chemical shifts of hydrogen halides, mercury dihalides and tungsten hexahalides and tetraoxides. The SFR terms were shown to strongly couple with the SO terms,

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affecting significantly the chemical shifts of heavy elements, Hg in particular. The SFR effects alone were rather small due to the locality of the effect.

The SO–UHF method is an approximate method, with incomplete inclusion of the spin–dipolar term, which is small for light nuclei [5]. To correct this defect, the generalized UHF (GUHF) method, which includes the SO interaction and the SFR terms (SO–GUHF) was developed [15]. The GUHF method is a quasi-relativistic two-component method in the mean-field approximation. Recently, Fukui et al. [16] have presented a gauge-invariant formalism which includes the magnetic vector potentials in the spin–orbit operator, but the additional terms were shown to be numerically quite small in practice. Malkin and coworkers [17,18] later showed the importance of the SO effect in density functional studies of nuclear magnetic shielding constants.

In view of the importance of the relativistic effects on magnetic shielding constants [5–15], four-component 'fully' relativistic theory should be formulated and applied to heavy atoms and to molecules which contain heavy atoms. In general, for systems consisting only of light elements, the non-relativistic Schrödinger equation satisfies the major postulates in calculating magnetic shielding constants [19] and relativistic effects, primarily the SO effect, are well incorporated by the lowest-order $(1/c^2)$ relativistic perturbation theory [5]. However, for systems containing heavy elements, four-component relativistic calculations are desirable since the relativistic effects in these systems are large and essential for describing their electronic states. However, fully relativistic calculations of magnetic shielding constants have never been carried out for polyatomic systems, although the theory itself, employing the sum-over-states formalism [1–3], has been proposed by several groups [1–3].

In this Letter, we present a four-component fully relativistic formulation of magnetic shielding in the framework of matrix Dirac–Fock finite perturbation (DF–FP) self-consistent field (SCF) theory. We explicitly deal with the four-component spinor solutions of the Dirac–Coulomb or Dirac–Coulomb–Breit many-body Hamiltonian. We investigate by this method the effects of the Dirac current and the Breit interaction on the magnetic shielding constants and calculate the chemical shifts of the noble gas atoms, He through Xe, and also of H_2, HF and HCl. Further applications of the DF–FP theory to calculations of magnetic shielding constants will be prevented elsewhere.

2. Theory

2.1. The relativistic Hamiltonian

The relativistic many-body Hamiltonian for atoms and molecules cannot be expressed in closed form. The reasons have to do with establishing covariance in the multiparticle system and with the separation of the electrons and the particle of interest, from the positrons, which are ignored. Nevertheless, relativistic mean-field and many-body theories may be developed by employing an effective Hamiltonian expressed in terms of an effective electron–electron interaction derived from QED.

In c-number theory, the starting point for our development of DF–FP theory is the so-called no-pair Dirac–Coulomb–Breit (DCB) Hamiltonian prescribed by Sucher [20] and Mittleman [21]. In the presence of the magnetic vector potential, the effective many-body Hamiltonian is given by

$$H_+^{\mathrm{DCB}}(\mathbf{B}_0) = \sum_i \left[c\boldsymbol{\alpha}\cdot(\mathbf{P}_i + \mathbf{A}_i) + \beta' c^2 + \sum_n V_n(i) \right] + L_+ \left[\tfrac{1}{2} \sum_{i\neq j} \left\{ \frac{1}{r_{ij}} + B_{ij} \right\} \right] L_+ \qquad (1)$$

where c is the speed of light and α and β' are the Dirac matrices. V_n is the nuclear attraction term due to the nucleus n. $L_+ = \Lambda_+(1)\Lambda_+(2)\ldots\Lambda_+(n)$ with Λ_+ the projection operator onto the space spanned by the positive-energy eigenfunctions of the matrix DF equation [20,21]. The projection operator takes into account the field-theoretic condition that the negative-energy states are filled. Throughout this study, atomic units are used and thus the speed of light is taken to be 137.0359895 au.

In the Coulomb gauge, B_{ij} represents the frequency-independent Breit interaction and is given by

$$B_{ij} = -\tfrac{1}{2r_{ij}} \left\{ \boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j + \left[(\boldsymbol{\alpha}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\alpha}_j\cdot\mathbf{r}_{ij})/r_{ij}^2 \right] \right\} \qquad (2)$$

The first and second terms are the magnetic part and the retardation part, respectively. The addition of B_{ij} to the instantaneous Coulomb operator in the effective electron–electron interaction introduces the leading effects of the transverse photon exchange in QED. It also provides covariance of the effective many-body Hamiltonian to first order and increases accuracy in inner-shell binding energies [20–22].

The vector potential $\mathbf{A}_i$ arising from a uniform external field $\mathbf{B}_0$ and the nuclear magnetic moment of the nth nucleus μ_n is given by

$$\mathbf{A}_i = \tfrac{1}{2}\mathbf{B}_0 \times (\mathbf{r}_i - \mathbf{d}) + \sum_n c^{-2}\mu_n \times \mathbf{r}_{ni} a_n(r_{ni}) \quad (3)$$

We assume that the nuclei have spherically symmetric shapes and uniform distribution of magnetic moment [23]. Thus $a_n(r_{ni})$ is a purely radial function with respect to the center of nucleus n and has the form [23,24],

$$a_n(r_{ni}) = \frac{1}{R_n^3} \qquad \text{if } r_{ni} < R_n \quad (4a)$$

$$a_n(r_{ni}) = \frac{1}{r_{ni}^3} \qquad \text{if } r_{ni} > R_n \quad (4b)$$

where R_n is the radius of the nucleus n and r_{ni} is the distance between the electron and the center of the nucleus n. $\mathbf{d}$ denotes the gauge origin. For $r_{ni} < R_n$, the radial function $a_n(r_{ni})$ is constant as shown in Eq. (4a).

In c-number theory, the magnetic field is treated classically by the interaction of a Dirac particle with an external classical electromagnetic field characterized by its potential $\mathbf{A}$. In the no-pair DCB Hamiltonian, there is a single perturbation $c\alpha \cdot \mathbf{A}$ which is linear in $\mathbf{A}$, whereas the perturbation in the non-relativistic approximation to the Dirac equation is quadratic in $\mathbf{A}$.

2.2. Magnetic shielding constant

The magnetic shielding constant σ_{tu} ($t, u = x, y, z$) is given by Ramsey [25] as,

$$\sigma_{n,tu} = \left.\frac{\partial^2 E}{\partial B_{0t}\partial \mu_{nu}}\right|_{B_{0t}=\mu_{nu}=0} \quad (5)$$

where E is the total N-electron DF energy. Expanding the no-pair DCB Hamiltonian in powers of $\mathbf{B}_0$ and μ_n, we obtain

$$H_+^{\mathrm{DCB}}(\mathbf{B}_0) = H_+^{\mathrm{DCB}(0,0)} + \sum_t B_{0t} H_t^{(1,0)} + \sum_n \sum_t \mu_{nt} H_{nt}^{(0,1)} \quad (6)$$

where $H_+^{\mathrm{DCB}(0,0)}$ is the DCB Hamiltonian in the absence of the $\mathbf{B}_0$ field and the other terms are defined as

$$H_t^{(1,0)} = \sum_i \tfrac{1}{2} c\left[(\mathbf{r}_i - \mathbf{d}) \times \alpha_i\right]_t, \quad (7)$$

$$H_{nt}^{(0,1)} = \tfrac{1}{c}\sum_i a_n(r_{ni})(\mathbf{r}_{ni} \times \alpha_i)_t. \quad (8)$$

Using the Hellmann–Feynman theorem, Eq. (5) is modified as

$$\sigma_{n,tu} = \frac{\partial}{\partial B_{0t}}\left[\left\langle \Phi^{\mathrm{DF}}(B_{0t}) \middle| H_{nu}^{(0,1)} \middle| \Phi^{\mathrm{DF}}(B_{0t}) \right\rangle\right]_{B_{0t}=0}, \quad (9)$$

and this is computed by the finite perturbation method.

In the present study, both unperturbed and perturbed N-electron wavefunctions, $\Phi^{\mathrm{DF}}(0)$ and $\Phi^{\mathrm{DF}}(\mathbf{B}_0)$, are approximated by a single Slater determinant of molecular DF spinors, $\phi^{\mathrm{DF}}(0)$ and $\phi^{\mathrm{DF}}(\mathbf{B}_0)$, respectively. The molecular DF spinors perturbed by the presence of the $\mathbf{B}_0$ field $\phi^{\mathrm{DF}}(\mathbf{B}_0)$ satisfy the DF–FP SCF equation,

$$\left[c\alpha \cdot \mathbf{P} + \beta' c^2 + \sum_n V_n + \mathbf{J} - \mathbf{K} + \tfrac{1}{2} c B_{0t}\{(\mathbf{r} - \mathbf{d}) \times \alpha\}_t\right]\phi_i^{\mathrm{DF}} = \varepsilon_i \phi_i^{\mathrm{DF}}, \quad (10)$$

where $\mathbf{J}$ and $\mathbf{K}$ are Coulomb and exchange operators, respectively.

The term $H_t^{(1,0)}$ (Eq. (7)) in the DF–FP SCF equation contains the spin-dependent term which lifts the spinor degeneracy in the presence of the $\mathbf{B}_0$ field. Consequently, one must solve the generalized unrestricted form of the matrix DF–FP SCF equation to account for the effects of the $\mathbf{B}_0$ field on the Kramers' spinor pairs.

In terms of the molecular DF spinors obtained by solving the matrix DF–FP equation, the magnetic

shielding tensor for the nucleus n can be expressed explicitly in the form,

$$\sigma_{tu} = \frac{\partial}{\partial B_{0t}} \left[\frac{1}{c} \sum_{i}^{\text{occ}} \langle \phi_i^{\text{DF}}(B_{0t}) | a_N(r_{Ni}) \times (\mathbf{r}_{Ni} \times \alpha)_u | \phi_i^{\text{DF}}(B_{0t}) \rangle \right]_{B_0=0} \quad (11)$$

Because we employ a fully relativistic formulation in terms of Dirac four-component spinors, all the relativistic and non-relativistic contributions to the magnetic shielding tensors are included in a single term of Eq. (11). The several contributing terms in the two-component formulation [1,5,12] arise from the decoupling of the upper and lower components of the Dirac four-spinors.

A major advantage of our theory over previous ones [1–3] is that the (positron-like) negative energy states do not appear explicitly in the evaluation of the magnetic shielding constant. Previous relativistic theories of NMR chemical shifts have used a sum-over-states perturbation formulation [1–3]. An undesirable feature of such formulations is that contributions from the negative-energy states having energies less than $-2c^2$ were as important as those arising from positive-energy states and the negative-energy states are difficult to handle computationally [1]. The DF–FP method employed in the present study avoids the explicit appearance of negative-energy states.

3. Computation

The matrix DF–FP procedure has been incorporated into the MOLFDIR suite of programs [26]. The bond distances used for H_2, HF, and HCl are those of Ref. [5]. The nuclei are approximated by a finite spherical model [24]. The atomic mass numbers used for He, Ne, Ar, Kr, Xe, F, Cl, Br, I and H are 4.0026, 20.179, 39.948, 83.80, 131.29, 18.998, 35.453, 79.904, 126.90 and 1.0079, respectively, and they are quite insensitive to the magnetic shielding constant.

The basis sets used in our calculations are as follows. For the large component molecular DF spinors, uncontracted gaussian functions, optimized by the non-relativistic calculations, have been used. The small component basis sets include the first derivatives of the large component basis functions so as to satisfy the condition of 'kinetic balance' [26,27]. The large component basis sets for He, Ne, Ar, Kr and Xe, respectively, were the (10s), (14s9p), (17s12p), (13s9p5d), and (15s11p5d) basis sets of Csizmadia et al. [28]. For H, F and Cl in the hydrogen halides, (3s), (6s3p) and (9s6p) sets [28], respectively, were used. For H in the hydrogen molecule, (4s), (4s4p) and (10s5p) sets [28] were employed to examine basis set dependence.

4. Results and discussion

To test our method, we have computed the magnetic shielding constants of the noble gas atoms, He through Xe. The results are shown in Table 1. The Dirac–Fock–Coulomb (DFC) calculation always gives a larger shielding constant than does Dirac–Fock–Breit (DFB), though their differences are not significant. In the Xe atom, the difference between DFC and DCB is 10 ppm. However, the differences between the DF and non-relativistic results are significant. Since the non-relativistic HF calculations are done in the same basis set to expand the large component DF spinors, these differences are almost solely due to relativistic effects. They are about 280 ppm and 1020 ppm in Kr and Xe, although quite small in He. The shielding constants become larger in the DF calculations than in the non-relativistic ones. This trend is also reproduced in calculations by the relativistic random phase approximation (RRPA) [29], though the RRPA gives much larger values for

Table 1
Magnetic shielding constants for noble-gas atoms (in ppm)

Atom	DFC	DFB	Non-relativistic[a]	RRPA[b]
He	59.92	59.92	59.90	59.95
Ne	557.04	556.83	552.27	558.6
Ar	1268.60	1267.78	1237.60	1276
Kr	3525.49	3521.52	3245.61	3598
Xe	6660.91	6650.79	5642.16	7040

[a] Non-relativistic calculations using the same basis set employed in the DF calculations.
[b] Relativistic calculations obtained by the random-phase approximation; Ref. [29].

Table 2
Magnetic shielding constants for H_2, HF and HCl (in ppm)

Molecule	DFC	DFB	Non-relativistic[a]	Experimental
H_2[b]				
H(4s)	26.630	26.630	26.680	26.689
H(4s4p)	26.434	26.434	26.555	26.689
H(10s5p)	26.339	26.339	26.444	26.689
HF[c]				
H	24.11	24.11	31.58	29.2
F	409.57	409.46	418.1	410
HCl[c]				
H	25.01	25.01	33.36	31.8
Cl	1028.15	1027.72	961.2	950

[a]Non-relativistic calculations using the same basis set employed in the DF calculations.
[b]The gauge center is located at the center of the H–H bond.
[c]The gauge center is located at the halogen atom.

the shielding constants than do the DF calculations. The differences arise from methods and basis sets; the difference produced by the finite nucleus approximation is small.

Our method has also been applied to diatomic molecules. The magnetic shielding constants of H, F and Cl in H_2, HF and HCl are listed in Table 2. The DFC and DCB calculations give essentially the same results as above. The agreement between experiment and the DF results is reasonable. The differences between the DF and non-relativistic calculations are meaningful even in these molecules for both proton and halogen nuclei. The trend of the relativistic effects is not constant, in contrast with the noble-gas atoms. The basis set dependence in the magnetic shielding constant of H in H_2 is moderate, but the shielding constant gradually departs from the experimental value as the basis set is improved. In comparison with the non-relativistic result, the relativistic effect becomes large as p-type basis functions are added.

5. Conclusion

A formulation for fully relativistic calculation of the magnetic shielding constant is given, based on four-component no-pair DFC and DFB theory. In this formalism, the shielding constant is expressed as a single term, rather than the two to four terms of the non-relativistic and quasi-relativistic theories [5,11], i.e. diamagnetic, paramagnetic, spin–dipolar, and Fermi contact terms. In adopting the finite perturbation method, we have avoided inclusion of the positron states in the formulation, an advantage over the sum-over-state formalism.

The applications to the noble gas atoms, He to Xe have shown that the relativistic effect is significant for the heavy atoms Kr and Xe. The Breit term is shown to be small for the shielding constant. The results for the small diatomics, H_2, HF and HCl show that the Breit term gives a difference only for the F and Cl shielding constants. However, relativistic effects are important for both hydrogen and the halogens.

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