

## ARTICLES

## A closed-shell coupled-cluster treatment of the Breit–Pauli first-order relativistic energy correction

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First-order relativistic corrections to the energy of closed-shell molecular systems are calculated, using all terms in the two-component Breit–Pauli Hamiltonian. In particular, we present the first implementation of the two-electron Breit orbit–orbit integrals, thus completing the first-order relativistic corrections within the two-component Pauli approximation. Calculations of these corrections are presented for a series of small and light molecules, at the Hartree–Fock and coupled-cluster levels of theory. Comparisons with four-component Dirac–Coulomb–Breit calculations demonstrate that the full Breit–Pauli energy corrections represent an accurate approximation to a fully relativistic treatment of such systems. The Breit interaction is dominated by the spin–spin interaction, the orbit–orbit interaction contributing only about 10% to the total two-electron relativistic correction in molecules consisting of light atoms. However, the relative importance of the orbit–orbit interaction increases with increasing nuclear charge, contributing more than 20% in  $\text{H}_2\text{S}$ . © 2004 American Institute of Physics. [DOI: 10.1063/1.1788634]

### I. INTRODUCTION

A well-established method for the calculation of relativistic corrections to molecular electronic energies is first-order perturbation theory, using the one-electron Pauli Hamiltonian—in particular, the mass-velocity and one-electron Darwin operators. This approach, which is often referred to as the Cowan–Griffin method,<sup>1</sup> has been successful for light systems, recovering most of the relativistic correction at little or no cost (even though its use may be problematic due to a divergent behavior arising from the mass-velocity term<sup>2,3</sup>). Indeed, applied at the Hartree–Fock level to molecules with light atoms, the Cowan–Griffin method is usually not in error by more than 10% with respect to the full relativistic correction, as calculated by the full configuration-interaction (FCI) method in the same basis, using all first-order relativistic terms in the Breit–Pauli approximation—that is, all terms of order  $O(c^{-2})$ . This is illustrated in Table I, where various first-order relativistic corrections are displayed for the  $\text{H}_2\text{S}$  molecule, both at the Hartree–Fock level and at the highly correlated coupled-cluster singles-and-doubles (triples) CCSD(T)(full) level (to mimic FCI). To go beyond the Cowan–Griffin Hartree–Fock method, we should take into account both the effect of electron correlation on the relativistic corrections and the effect of the terms in the

Breit–Pauli Hamiltonian that are not included in the Cowan–Griffin method. In general, each effect is equally important and neither can be neglected if we want to improve on the standard Cowan–Griffin Hartree–Fock approach.<sup>4</sup> In the present paper, we compute all first-order corrections of the Breit–Pauli Hamiltonian at the coupled-cluster level, for closed-shell molecules containing light atoms (not heavier than argon).

Beyond the Cowan–Griffin model, we only need to consider the two-electron Darwin term to arrive at the full Pauli relativistic correction of a closed-shell system. In recent years, such calculations have, for example, been carried out by Tennyson and co-workers in their accurate studies of the rovibrational spectra of triatomics.<sup>5,6</sup> However, the Pauli approximation does not exhaust all relativistic terms of order  $c^{-2}$ . In the Breit Hamiltonian, there are three additional terms: the two-electron spin–spin and orbit–orbit operators, which contribute to the first-order energy of a closed-shell system, and the spin–orbit operator, which makes no such contribution. The nonzero spin–spin contribution is trivially related to the two-electron Darwin term, being twice as large but of the opposite sign.<sup>7–9</sup> The remaining orbit–orbit contribution is more complicated, however, requiring the coding of new integrals whose permutational symmetry is different

TABLE I. First-order Breit–Pauli corrections (in  $E_h$ ) for  $H_2S$ . At the equilibrium geometry and in the CVDZ basis of Ref. 4.

Correction	Hartree–Fock	CCSD(T)(full)
Mass-velocity	−4.549	−4.551
One-electron Darwin	3.474	3.474
Two-electron Darwin	−0.034	−0.033
Spin–spin	0.068	0.066
Orbit–orbit	0.019	0.018
Total	−1.022	−1.026

from that of the standard two-electron repulsion integrals. Up to now, no implementation of the orbit–orbit contribution has therefore been reported in the literature.

In this paper, we present an implementation of the Breit–Pauli orbit–orbit contribution to the first-order relativistic energy of closed-shell systems, enabling us to carry out the first calculations that include all relativistic corrections proportional to  $c^{-2}$ . Such calculations are carried out for a selected set of molecules, for which comparisons can be made with four-component Dirac–Coulomb–Breit results. We note that most four-component calculations do not use the full two-electron Breit Hamiltonian (in standard notation and atomic units),

$$\hat{H}^{B2} = \frac{1}{2} \sum_{i \neq j} r_{ij}^{-1} - \frac{1}{4} \sum_{i \neq j} (\boldsymbol{\alpha}_i \cdot r_{ij}^{-1} \boldsymbol{\alpha}_j + \boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij} r_{ij}^{-3} \mathbf{r}_{ij} \cdot \boldsymbol{\alpha}_j), \quad (1)$$

but either only the Coulomb two-electron operator or the Coulomb operator augmented with the Gaunt term, which corresponds to twice the first term in the second summation:  $\hat{H}^{\text{Gaunt}} = -1/2 \sum_{i \neq j} \boldsymbol{\alpha}_i \cdot r_{ij}^{-1} \boldsymbol{\alpha}_j$ . In the reduced two-component form of the Pauli approximation, we here use the full Breit operator, noting that the separate evaluation of the reduced Gaunt term is more difficult than evaluation of the full reduced Breit operator.

The remainder of this paper consists of three sections: In Sec. II, we discuss the Breit–Pauli Hamiltonian, presenting its constituent operators in second-quantized form and describing the evaluation of the corresponding integrals in the atomic-orbital (AO) basis. Next, in Sec. III, we present calculations on small and light molecular systems at the Hartree–Fock and CCSD levels of theory, comparing with the Dirac–Coulomb–Breit calculations of Ref. 4. Section IV concludes the paper.

## II. THEORY

### A. The Breit–Pauli Hamiltonian

The Breit–Pauli and Breit Hamiltonian operators are given by<sup>10–13</sup>

$$\hat{H}^{\text{BP}} = \hat{H}^{\text{NR}} + \hat{H}^{\text{MV}} + \hat{H}^{\text{D1}} + \hat{H}^{\text{D2}} + \hat{H}^{\text{SO1}} + \hat{H}^{\text{SO2}} + \hat{H}^{\text{Breit}}, \quad (2)$$

$$\hat{H}^{\text{Breit}} = \hat{H}^{\text{SoO}} + \hat{H}^{\text{OO}} + \hat{H}^{\text{SS}}, \quad (3)$$

where, in atomic units, we have introduced the field-free nonrelativistic Hamiltonian,

$$\hat{H}^{\text{NR}} = \frac{1}{2} \sum_i p_i^2 - \sum_{i,K} \frac{Z_K}{r_{iK}} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} + \frac{1}{2} \sum_{K \neq L} \frac{Z_K Z_L}{R_{KL}}, \quad (4)$$

the one-electron mass-velocity operator,

$$\hat{H}^{\text{MV}} = -\frac{1}{8c^2} \sum_i p_i^4, \quad (5)$$

the one- and two-electron Darwin operators, respectively,

$$\hat{H}^{\text{D1}} = \frac{\pi}{2c^2} \sum_{i,K} Z_K \delta(r_{iK}), \quad (6)$$

$$\hat{H}^{\text{D2}} = -\frac{\pi}{2c^2} \sum_{i \neq j} \delta(r_{ij}), \quad (7)$$

the one- and two-electron spin–orbit operators, respectively,

$$\hat{H}^{\text{SO1}} = \frac{1}{4c^2} \sum_{i,K} \frac{Z_K \boldsymbol{\sigma}_i \cdot (\mathbf{r}_{iK} \times \mathbf{p}_i)}{r_{iK}^3}, \quad (8)$$

$$\hat{H}^{\text{SO2}} = -\frac{1}{4c^2} \sum_{i \neq j} \frac{\boldsymbol{\sigma}_i \cdot (\mathbf{r}_{ij} \times \mathbf{p}_i)}{r_{ij}^3}, \quad (9)$$

and the Breit spin–other-orbit, orbit–orbit, and spin–spin operators, respectively,

$$\hat{H}^{\text{SoO}} = \frac{1}{2c^2} \sum_{i \neq j} \frac{\boldsymbol{\sigma}_i \cdot (\mathbf{r}_{ij} \times \mathbf{p}_j)}{r_{ij}^3}, \quad (10)$$

$$\hat{H}^{\text{OO}} = -\frac{1}{4c^2} \sum_{i \neq j} (\mathbf{p}_i \cdot r_{ij}^{-1} \mathbf{p}_j + \mathbf{p}_i \cdot \mathbf{r}_{ij} r_{ij}^{-3} \mathbf{r}_{ij} \cdot \mathbf{p}_j), \quad (11)$$

$$\hat{H}^{\text{SS}} = \frac{1}{8c^2} \sum_{i \neq j} \left[ \boldsymbol{\sigma}_i \cdot r_{ij}^{-3} \boldsymbol{\sigma}_j - 3 \boldsymbol{\sigma}_i \cdot \mathbf{r}_{ij} r_{ij}^{-5} \mathbf{r}_{ij} \cdot \boldsymbol{\sigma}_j - \frac{8\pi}{3} \delta(r_{ij}) \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \right]. \quad (12)$$

In these expressions, subscripts  $i$  and  $j$  are used for the electrons, whereas  $K$  and  $L$  are used for the nuclei. The nuclear charges are denoted by  $Z_K$ , the Pauli spin matrices by  $\boldsymbol{\sigma}_i$ , the conjugate momentum by  $\mathbf{p}_i$ , and the velocity of light by  $c \approx 137$  (a.u.). We also note that, when the two-electron Gaunt rather than Breit operator is used in Eq. (1), then the orbit–orbit operator takes the form<sup>12,13</sup>

$$\hat{H}_{\text{Gaunt}}^{\text{OO}} = -\frac{1}{2c^2} \sum_{i \neq j} [\mathbf{p}_i \cdot r_{ij}^{-1} \mathbf{p}_j + \pi \delta(r_{ij})]. \quad (13)$$

No other reduced two-component operators are affected by the use of the Gaunt rather than the full Breit operator.

For the evaluation of molecular integrals, the following expressions in terms of differential operators are more useful than those in Eqs. (8)–(12):

$$\hat{H}^{\text{SO1}} = \frac{i}{4c^2} \sum_{i,K} Z_K \boldsymbol{\sigma}_i \cdot (\nabla_i r_{iK}^{-1}) \times \nabla_i, \quad (14)$$

$$\hat{H}^{SO2} = -\frac{i}{4c^2} \sum_{i \neq j} \boldsymbol{\sigma}_i \cdot (\nabla_i r_{ij}^{-1}) \times \nabla_i, \quad (15)$$

$$\hat{H}^{SoO} = \frac{i}{2c^2} \sum_{i \neq j} \boldsymbol{\sigma}_i \cdot (\nabla_i r_{ij}^{-1}) \times \nabla_j, \quad (16)$$

$$\hat{H}^{OO} = \frac{1}{4c^2} \sum_{i \neq j} \nabla_i^T [(\mathbf{I}_3 \Delta_i - \nabla_i \nabla_i^T) r_{ij}] \nabla_j, \quad (17)$$

$$\hat{H}^{SS} = \frac{1}{8c^2} \sum_{i \neq j} \boldsymbol{\sigma}_i^T [(\mathbf{I}_3 \Delta_i - \nabla_i \nabla_i^T) r_{ij}^{-1}] \boldsymbol{\sigma}_j, \quad (18)$$

where we have made use of the relations

$$(\mathbf{I}_3 \Delta - \nabla \nabla^T) r = \frac{\mathbf{I}_3 r^2 + \mathbf{r} \mathbf{r}^T}{r^3}, \quad (19)$$

$$(\mathbf{I}_3 \Delta - \nabla \nabla^T) r^{-1} = \frac{\mathbf{I}_3 r^2 - 3 \mathbf{r} \mathbf{r}^T}{r^5} - \frac{8\pi}{3} \delta(r). \quad (20)$$

The corresponding form of the Gaunt orbit–orbit operator, Eq. (13), is

$$\hat{H}_{\text{Gaunt}}^{OO} = \frac{1}{2c^2} \sum_{i \neq j} [\nabla_i^T r_{ij}^{-1} \nabla_j - \pi \delta(r_{ij})]. \quad (21)$$

The Breit spin–spin operator, Eq. (12), is often decomposed into the Fermi-contact (FC) and dipolar (DP) operators:

$$\hat{H}^{SS} = \hat{H}^{\text{FC}} + \hat{H}^{\text{DP}}, \quad (22)$$

where

$$\hat{H}^{\text{FC}} = -\frac{\pi}{3c^2} \sum_{i \neq j} \delta(r_{ij}) \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j = \frac{1}{12c^2} \sum_{i \neq j} (\Delta_i r_{ij}^{-1}) \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j, \quad (23)$$

$$\begin{aligned} \hat{H}^{\text{DP}} &= \frac{1}{8c^2} \sum_{i \neq j} (\boldsymbol{\sigma}_i \cdot r_{ij}^{-3} \boldsymbol{\sigma}_j - 3 \boldsymbol{\sigma}_i \cdot \mathbf{r}_{ij} r_{ij}^{-5} \mathbf{r}_{ij} \cdot \boldsymbol{\sigma}_j) \\ &= \frac{1}{8c^2} \sum_{ij} \boldsymbol{\sigma}_i^T \left[ \left( \frac{1}{3} \mathbf{I}_3 \Delta_i - \nabla_i \nabla_i^T \right) r_{ij}^{-1} \right] \boldsymbol{\sigma}_j. \end{aligned} \quad (24)$$

Whereas the Fermi-contact operator is isotropic, the dipolar spin–spin operator is traceless.

### B. Second-quantization representation of the operators

In terms of the singlet excitation operators

$$E_{pq} = a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}, \quad (25)$$

the nonrelativistic electronic Hamiltonian in Eq. (4) takes the following standard second-quantized form:

$$\begin{aligned} \hat{H}^{\text{NR}} &= -\frac{1}{2} \sum_{pq} \langle p | \Delta | q \rangle E_{pq} - \sum_{pq} \sum_K Z_K \langle p | r_K^{-1} | q \rangle E_{pq} \\ &\quad + \frac{1}{2} \sum_{pqrs} \langle pr | r_{12}^{-1} | qs \rangle (E_{pq} E_{rs} - \delta_{qr} E_{ps}) \\ &\quad + \frac{1}{2} \sum_{K \neq L} \frac{Z_K Z_L}{R_{KL}}, \end{aligned} \quad (26)$$

where we use the following notation for the one- and two-electron integrals:

$$\langle p | \hat{h} | q \rangle = \int \phi_p^*(\mathbf{r}) \hat{h} \phi_q(\mathbf{r}) d\mathbf{r}, \quad (27)$$

$$\begin{aligned} \langle pr | r_{12}^{-1} | qs \rangle \\ = \int \int \phi_p^*(\mathbf{r}_1) \phi_r^*(\mathbf{r}_2) r_{12}^{-1} \phi_q(\mathbf{r}_1) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (28)$$

In the same notation, the singlet mass-velocity and Darwin operators Eqs. (5)–(7) become

$$\hat{H}^{\text{MV}} = -\frac{1}{8c^2} \sum_{pq} \langle p | \Delta^2 | q \rangle E_{pq}, \quad (29)$$

$$\hat{H}^{\text{D1}} = \frac{\pi}{2c^2} \sum_K Z_K \sum_{pq} \langle p | \delta(r_K) | q \rangle E_{pq}, \quad (30)$$

$$\hat{H}^{\text{D2}} = -\frac{\pi}{2c^2} \sum_{pqrs} \langle pr | \delta(r_{12}) | qs \rangle (E_{pq} E_{rs} - \delta_{qr} E_{ps}), \quad (31)$$

whereas the triplet spin–orbit operators Eqs. (14)–(16) take the form

$$\hat{H}^{SO1} = \frac{i}{4c^2} \sum_K Z_K \sum_{pq} \langle p | (\nabla r_K^{-1}) \times \nabla | q \rangle \cdot \mathbf{T}_{pq}, \quad (32)$$

$$\begin{aligned} \hat{H}^{SO2} &= -\frac{i}{4c^2} \sum_{pqrs} \langle pr | (\nabla_1 r_{12}^{-1}) \times \nabla_1 | qs \rangle \\ &\quad \cdot (\mathbf{T}_{pq} E_{rs} - \delta_{qr} \mathbf{T}_{ps}), \end{aligned} \quad (33)$$

$$\begin{aligned} \hat{H}^{SoO} &= \frac{i}{2c^2} \sum_{pqrs} \langle pr | (\nabla_1 r_{12}^{-1}) \times \nabla_2 | qs \rangle \\ &\quad \cdot (\mathbf{T}_{pq} E_{rs} - \delta_{qr} \mathbf{T}_{ps}), \end{aligned} \quad (34)$$

where we have introduced vectors containing the Cartesian triplet excitation operators:

$$T_{pq}^x = \frac{1}{2} (a_{p\alpha}^\dagger a_{q\beta} + a_{p\beta}^\dagger a_{q\alpha}), \quad (35)$$

$$T_{pq}^y = \frac{1}{2i} (a_{p\alpha}^\dagger a_{q\beta} - a_{p\beta}^\dagger a_{q\alpha}), \quad (36)$$

$$T_{pq}^z = \frac{1}{2} (a_{p\alpha}^\dagger a_{q\alpha} - a_{p\beta}^\dagger a_{q\beta}). \quad (37)$$

In second quantization, the orbit–orbit operator, Eq. (17), and the spin–spin operator, Eq. (18), are given by

$$\hat{H}^{OO} = \frac{1}{4c^2} \sum_{pqrs} \langle pr | \nabla_1^T [(\mathbf{I}_3 \Delta_1 - \nabla_1 \nabla_1^T) r_{12}] \nabla_2 | qs \rangle \times (E_{pq} E_{rs} - \delta_{qr} E_{ps}), \quad (38)$$

$$\hat{H}^{SS} = \frac{1}{8c^2} \sum_{pqrs} \sum_{\mu\nu} \langle pr | [(\mathbf{I}_3 \Delta_1 - \nabla_1 \nabla_1^T) r_{12}^{-1}]_{\mu\nu} | qs \rangle \times (4T_{pq}^\mu T_{rs}^\nu - \delta_{\mu\nu} \delta_{qr} E_{ps}). \quad (39)$$

We note that the corresponding Gaunt version of orbit-orbit operator, Eq. (21), is given by

$$\hat{H}_{\text{Gaunt}}^{OO} = \frac{1}{2c^2} \sum_{pqrs} \langle pr | \nabla_1^T r_{12}^{-1} \nabla_2 - \pi \delta(r_{12}) | qs \rangle \times (E_{pq} E_{rs} - \delta_{qr} E_{ps}), \quad (40)$$

while the Fermi-contact and dipolar contributions, Eqs. (23) and (24), to the spin-spin operator may be written in the form

$$\hat{H}^{\text{FC}} = -\frac{\pi}{3c^2} \sum_{pqrs} \langle pr | \delta(r_{12}) | qs \rangle (4\mathbf{T}_{pq} \cdot \mathbf{T}_{rs} - 3\delta_{qr} E_{ps}), \quad (41)$$

$$\hat{H}^{\text{DP}} = \frac{1}{2c^2} \sum_{pqrs} \mathbf{T}_{pq}^T \langle pr | \left[ \left( \frac{1}{3} \mathbf{I}_3 \Delta_1 - \nabla_1 \nabla_1^T \right) r_{12}^{-1} \right] | qs \rangle \mathbf{T}_{rs}. \quad (42)$$

There is no contribution from the singlet excitation operators to the traceless dipolar spin-spin operator.

In passing, we note that, for a general triplet two-electron operator of the form

$$\hat{H}_Q = \frac{1}{8c^2} \sum_{i \neq j} \boldsymbol{\sigma}_i^T \mathbf{Q}_{ij} \boldsymbol{\sigma}_j, \quad (43)$$

the corresponding second-quantized operator is given by

$$\hat{H}_Q = \frac{1}{8c^2} \sum_{pqrs} \sum_{\mu\nu} \langle pr | Q_{\mu\nu} | qs \rangle \left( 4T_{pq}^\mu T_{rs}^\nu - \delta_{qr} \delta_{\mu\nu} E_{ps} - 2i \delta_{qr} \sum_{\lambda} \epsilon_{\mu\nu\lambda} T_{ps}^\lambda \right), \quad (44)$$

where  $\epsilon_{\mu\nu\lambda}$  is the unit antisymmetric tensor. If Eq. (43) is spatially symmetric  $\mathbf{Q} = \mathbf{Q}^T$ , then the terms linear in the triplet excitation operators vanish; conversely, if it is antisymmetric  $\mathbf{Q} = -\mathbf{Q}^T$ , then only the linear triplet terms contribute.

### C. Expectation values for closed-shell states

Because of the presence of the triplet excitation operators in the Breit-Pauli Hamiltonian Eq. (2), many terms vanish as we take the expectation value of this Hamiltonian for a closed-shell electronic state. To identify the zero contributions and symmetries among the nonzero ones, it is expedient to consider the triplet excitation operators in the spherical-harmonic spin-tensor form:

$$T_{pq}^{1,1} = -a_{p\alpha}^\dagger a_{q\beta}, \quad (45)$$

$$T_{pq}^{1,0} = \frac{1}{\sqrt{2}} (a_{p\alpha}^\dagger a_{q\alpha} - a_{p\beta}^\dagger a_{q\beta}), \quad (46)$$

$$T_{pq}^{1,-1} = a_{p\beta}^\dagger a_{q\alpha}, \quad (47)$$

to which the Cartesian triplet excitation operators, Eqs. (35)–(37), multiplied by  $\sqrt{2}$  are related by a unitary transformation:

$$\sqrt{2} \begin{pmatrix} T_{pq}^x \\ T_{pq}^y \\ T_{pq}^z \end{pmatrix} = \begin{pmatrix} -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} T_{pq}^{1,1} \\ T_{pq}^{1,-1} \\ T_{pq}^{1,0} \end{pmatrix}. \quad (48)$$

From the Wigner-Eckart theorem, we note that, for a closed-shell singlet electronic state  $|cs\rangle$ , the spin-tensor excitation operators satisfy the relations

$$\begin{aligned} \langle cs | T_{pq}^{1,0} T_{rs}^{1,0} | cs \rangle &= -\langle cs | T_{pq}^{1,1} T_{rs}^{1,-1} | cs \rangle \\ &= -\langle cs | T_{pq}^{1,-1} T_{rs}^{1,1} | cs \rangle \neq 0, \end{aligned} \quad (49)$$

all other products of two triplet spin-tensor operators and all single triplet operators having zero expectation values. Therefore, for some general operator  $\mathbf{T}_{pq}^T \mathbf{R}_{pqrs} \mathbf{T}_{rs}$ , where  $\mathbf{T}_{pq}$  and  $\mathbf{T}_{rs}$  contain the Cartesian triplet excitation operators, only its isotropic component  $R_{pqrs} = 1/3 \text{Tr} \mathbf{R}_{pqrs}$  contributes to the expectation value of a singlet state

$$\sum_{pqrs} \langle cs | \mathbf{T}_{pq}^T \mathbf{R}_{pqrs} \mathbf{T}_{rs} | cs \rangle = \frac{3}{2} \sum_{pqrs} R_{pqrs} \langle cs | T_{pq}^{1,0} T_{rs}^{1,0} | cs \rangle. \quad (50)$$

Taking the expectation value of  $\hat{H}^{SS}$ , we then find that only the isotropic Fermi-contact term contributes for singlet states

$$\begin{aligned} \langle cs | \hat{H}^{SS} | cs \rangle &= -\frac{\pi}{c^2} \sum_{pqrs} \langle pr | \delta(r_{12}) | qs \rangle \\ &\quad \times \langle cs | 2T_{pq}^{1,0} T_{rs}^{1,0} - \delta_{qr} E_{ps} | cs \rangle. \end{aligned} \quad (51)$$

Next, taking advantage of the special permutational symmetries among the indices of the integral  $\langle pr | \delta(r_{12}) | qs \rangle = \int \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}) \phi_r^*(\mathbf{r}) \phi_s(\mathbf{r}) d\mathbf{r}$ , we find that, for singlet states, the expectation value of the two-electron spin-spin operator may be expressed entirely in terms of singlet excitation operators

$$\langle cs | \hat{H}^{SS} | cs \rangle = \frac{\pi}{c^2} \sum_{pqrs} \langle pr | \delta(r_{12}) | qs \rangle \langle cs | E_{pq} E_{rs} - \delta_{qr} E_{ps} | cs \rangle. \quad (52)$$

Finally, comparing this expression with the singlet two-electron Darwin operator in Eq. (31), we conclude that, for singlet states, the expectation values of the two-electron spin-spin and Darwin operators are related in the following simple manner:

$$\langle cs | \hat{H}^{SS} | cs \rangle = -2 \langle cs | \hat{H}^{\text{D}2} | cs \rangle, \quad (53)$$

giving the following expression for the expectation value of the Breit operator for closed-shell electronic state:

$$\langle \text{cs} | \hat{H}^{\text{Breit}} | \text{cs} \rangle = \langle \text{cs} | \hat{H}^{\text{OO}} - 2\hat{H}^{\text{D2}} | \text{cs} \rangle, \quad (54)$$

with no contributions from the spin-other-orbit and dipolar spin–spin operators. Consequently, the expectation value of the total Breit–Pauli operator may be calculated as

$$\begin{aligned} \langle \text{cs} | \hat{H}^{\text{BP}} | \text{cs} \rangle &= \langle \text{cs} | \hat{H}^{\text{NR}} | \text{cs} \rangle \\ &+ \langle \text{cs} | \hat{H}^{\text{MV}} + \hat{H}^{\text{D1}} - \hat{H}^{\text{D2}} + \hat{H}^{\text{OO}} | \text{cs} \rangle, \end{aligned} \quad (55)$$

with a negative sign on the two-electron Darwin term. Finally, when the Gaunt operator rather than the full Breit operator is used, we need only replace  $\hat{H}^{\text{OO}}$  by  $\hat{H}_{\text{Gaunt}}^{\text{OO}}$  in Eq. (55). Since the contact term in  $\hat{H}_{\text{Gaunt}}^{\text{OO}}$ , see Eq. (40), is exactly equal to the two-electron Darwin operator  $\hat{H}^{\text{D2}}$ , Eq. (31), we find that there is no contact contribution to the expectation value of the  $\hat{H}^{\text{BP}}$  operator for closed-shell states, Eq. (55), if the Breit operator is replaced by the Gaunt operator.

#### D. Atomic-orbital integral evaluation

The mass-velocity and Darwin operators, Eqs. (29)–(31), present no problems but are given here for completeness. Expanding the molecular integrals in AOs, we obtain (assuming real orbitals)

$$\hat{H}^{\text{MV}} = \sum_{pq} \sum_{ab} C_{pa} C_{qb} h_{ab}^{\text{MV}} E_{pq}, \quad (56)$$

$$\hat{H}^{\text{D1}} = \sum_{pq} \sum_{ab} C_{pa} C_{qb} h_{ab}^{\text{D1}} E_{pq}, \quad (57)$$

$$\hat{H}^{\text{D2}} = \frac{1}{2} \sum_{pqrs} \sum_{abcd} C_{pa} C_{qb} C_{rc} C_{sd} h_{abcd}^{\text{D2}} (E_{pq} E_{rs} - \delta_{qr} E_{ps}), \quad (58)$$

where the  $C_{pa}$  are the real molecular-orbital (MO) expansion coefficients and where the one- and two-electron (AO) integrals are given by

$$h_{ab}^{\text{MV}} = -\frac{1}{8c^2} \Delta_A \Delta_B \langle a | b \rangle, \quad (59)$$

$$h_{ab}^{\text{D1}} = \frac{\pi}{2c^2} \sum_K Z_K \langle a | \delta(r_K) | b \rangle, \quad (60)$$

$$h_{abcd}^{\text{D2}} = -\frac{\pi}{c^2} \langle ac | \delta(r_{12}) | bd \rangle. \quad (61)$$

These integrals, which are easily evaluated by standard techniques such as the McMurchie–Davidson scheme,<sup>14</sup> are symmetric with permutations to any two of the indices  $a, b, c,$  and  $d$ .

Next, considering the Breit–Pauli spin–orbit operators, Eqs. (32)–(34)

$$\hat{H}^{\text{SO1}} = \sum_{pq} \sum_{ab} C_{pa} C_{qb} \mathbf{h}_{ab}^{\text{SO1}} \cdot \mathbf{T}_{pq}, \quad (62)$$

$$\begin{aligned} \hat{H}^{\text{SO2}} &= \frac{1}{2} \sum_{pqrs} \sum_{abcd} C_{pa} C_{qb} C_{rc} C_{sd} \mathbf{h}_{abcd}^{\text{SO2}} \\ &\cdot (\mathbf{T}_{pq} E_{rs} - \delta_{qr} \mathbf{T}_{ps}), \end{aligned} \quad (63)$$

$$\begin{aligned} \hat{H}^{\text{SoO}} &= \frac{1}{2} \sum_{pqrs} \sum_{abcd} C_{pa} C_{qb} C_{rc} C_{sd} \mathbf{h}_{abcd}^{\text{SoO}} \\ &\cdot (\mathbf{T}_{pq} E_{rs} - \delta_{qr} \mathbf{T}_{ps}), \end{aligned} \quad (64)$$

we find that the AO integrals may be obtained as derivatives of the Coulomb integrals with respect to the AO centers  $A, B, C,$  and  $D$  as follows:

$$\mathbf{h}_{ab}^{\text{SO1}} = -\frac{i}{4c^2} \sum_K Z_K \nabla_A \times \nabla_B \langle a | r_K^{-1} | b \rangle, \quad (65)$$

$$\mathbf{h}_{abcd}^{\text{SO2}} = \frac{i}{2c^2} \nabla_A \times \nabla_B \langle ac | r_{12}^{-1} | bd \rangle, \quad (66)$$

$$\mathbf{h}_{abcd}^{\text{SoO}} = \frac{i}{c^2} \nabla_C \times \nabla_D \langle ac | r_{12}^{-1} | bd \rangle. \quad (67)$$

In deriving these expressions, we have made extensive use of the relations

$$\langle ac | (\nabla_{r_{12}}^{-1}) | bd \rangle = \nabla_P \langle ac | r_{12}^{-1} | bd \rangle = -\nabla_Q \langle ac | r_{12}^{-1} | bd \rangle, \quad (68)$$

$$\nabla_P = \nabla_A + \nabla_B, \quad \nabla_Q = \nabla_C + \nabla_D, \quad (69)$$

where  $\mathbf{P}$  and  $\mathbf{Q}$  are given by the expressions

$$\mathbf{P} = \frac{a\mathbf{A} + b\mathbf{B}}{a + b}, \quad \mathbf{Q} = \frac{c\mathbf{C} + d\mathbf{D}}{c + d}, \quad (70)$$

in terms of the positions  $\mathbf{A}, \mathbf{B}, \mathbf{C},$  and  $\mathbf{D}$  and the exponents  $a, b, c,$  and  $d$  of the four AOs in the two-electron integrals  $\langle ac | r_{12}^{-1} | bd \rangle$ . Note that, whereas the two-electron spin-own-orbit integrals, Eq. (66), are antisymmetric with respect to permutations of the indices  $ab$  of the first electron [like the one-electron spin–orbit integrals Eq. (65)] but symmetric with respect to permutations of the indices  $cd$  of the second electron, the two-electron spin-other-orbit integrals, Eq. (66), are symmetric with respect to permutations of  $ab$  but antisymmetric with respect to permutations of  $cd$ .

Using the same technique, we find that the AO integrals of the orbit–orbit and spin–spin Breit operators, Eqs. (38) and (39),

$$\begin{aligned} \hat{H}^{\text{OO}} &= \frac{1}{2} \sum_{pqrs} \sum_{abcd} C_{pa} C_{qb} C_{rc} C_{sd} h_{abcd}^{\text{OO}} \\ &\times (E_{pq} E_{rs} - \delta_{qr} E_{ps}), \end{aligned} \quad (71)$$

$$\begin{aligned} \hat{H}^{\text{SS}} &= \frac{1}{2} \sum_{pqrs} \sum_{abcd} C_{pa} C_{qb} C_{rc} C_{sd} [\mathbf{h}_{abcd}^{\text{SS}}]_{\mu\nu} \\ &\times (4T_{pq}^{\mu} T_{rs}^{\nu} - \delta_{\mu\nu} \delta_{qr} E_{ps}), \end{aligned} \quad (72)$$

may be computed as derivatives of the two-electron integrals  $\langle ac | r_{12} | bd \rangle$  and  $\langle ac | r_{12}^{-1} | bd \rangle$ :

$$h_{abcd}^{\text{OO}} = \frac{1}{2c^2} \nabla_A^T (\mathbf{I}_3 \Delta_P - \nabla_P \nabla_P^T) \nabla_C \langle ac | r_{12} | bd \rangle, \quad (73)$$

$$\mathbf{h}_{abcd}^{\text{SS}} = \frac{1}{4c^2} (\mathbf{I}_3 \Delta_P - \nabla_P \nabla_P^T) \langle ac | r_{12}^{-1} | bd \rangle. \quad (74)$$

In the Gaunt approximation Eq. (40), the orbit–orbit integrals are given by

$$[h_{\text{Gaunt}}^{\text{OO}}]_{abcd} = \frac{1}{c^2} \nabla_A^T \nabla_D \langle ac | r_{12}^{-1} | bd \rangle - \frac{\pi}{c^2} \langle ac | \delta(r_{12}) | bd \rangle, \quad (75)$$

rather than by Eq. (73) and all other integrals are unaffected.

Whereas the spin–spin integrals are symmetric in  $a$  and  $b$  and in  $c$  and  $d$ , the Breit orbit–orbit integrals are antisymmetric in the same pairs of indices, as follows for  $a$  and  $b$  from the identities:

$$\begin{aligned} (\nabla_A + \nabla_B)^T (\mathbf{I}_3 \Delta_P - \nabla_P \nabla_P^T) \\ = \nabla_P^T (\mathbf{I}_3 \Delta_P - \nabla_P \nabla_P^T) = \nabla_P^T \Delta_P - \Delta_P \nabla_P^T = \mathbf{0}^T. \end{aligned} \quad (76)$$

To establish the equivalent antisymmetry of  $c$  and  $d$ , we proceed in the same manner, using the translational invariance  $(\nabla_P + \nabla_Q) \langle ac | r_{12} | bd \rangle = \mathbf{0}$ . By contrast, in the Gaunt orbit–orbit integrals, there is no permutational symmetry between  $a$  and  $b$  nor between  $c$  and  $d$ . To summarize, we have established the following permutational symmetries of the AO spin–orbit, spin–spin, and (Breit) orbit–orbit integrals

$$\begin{aligned} \mathbf{h}_{ab}^{\text{SO1}} &= -\mathbf{h}_{ba}^{\text{SO1}}, \\ \mathbf{h}_{abcd}^{\text{SO2}} &= -\mathbf{h}_{bacd}^{\text{SO2}} = \mathbf{h}_{abdc}^{\text{SO2}} = -\mathbf{h}_{badc}^{\text{SO2}}, \\ \mathbf{h}_{abcd}^{\text{SoO}} &= \mathbf{h}_{bacd}^{\text{SoO}} = -\mathbf{h}_{abdc}^{\text{SoO}} = -\mathbf{h}_{badc}^{\text{SoO}}, \\ \mathbf{h}_{abcd}^{\text{SS}} &= \mathbf{h}_{bacd}^{\text{SS}} = \mathbf{h}_{abdc}^{\text{SS}} = \mathbf{h}_{badc}^{\text{SS}}, \\ \mathbf{h}_{abcd}^{\text{OO}} &= -\mathbf{h}_{bacd}^{\text{OO}} = -\mathbf{h}_{abdc}^{\text{OO}} = \mathbf{h}_{badc}^{\text{OO}}. \end{aligned} \quad (77)$$

In addition, the spin–spin and orbit–orbit integrals are symmetric with respect to permutations of  $ab$  and  $cd$ . Using these permutational symmetries as well as the relations Eq. (69), we find that the spin–orbit, spin–spin, and orbit–orbit integrals may be evaluated in a number of equivalent ways, as different derivatives with respect to the atomic centers **A**, **B**, **C**, and **D** or the centers **P** and **Q**.

### E. Coupled-cluster expectation values

We now discuss the evaluation of the first-order Breit–Pauli energy correction for a closed-shell singlet state using the coupled-cluster singles (CCS) model, CCSD model, and the CCSD perturbative triples [CCSD(T)] model. For these wave-function models, the evaluation of the molecular gradient for a closed-shell singlet case is described by Hald *et al.* in Ref. 15. As discussed below, the CCSD(T) Breit–Pauli energy correction of Eq. (55) may be calculated using a simplified version of the molecular-gradient expression given in Eq. (26) of Ref. 15. The CCSD energy correction is then obtained from the CCSD(T) expression by omitting all terms

that involve triples amplitudes; likewise, the CCS gradient is obtained by omitting all terms that involve doubles and triples amplitudes.

The main difference between a molecular-gradient calculation and the evaluation of the Breit–Pauli energy correction is that perturbation-dependent AOs are used for the molecular gradient, whereas fixed AOs are used for the energy correction. The contributions to the molecular gradient that involve overlap derivatives therefore do not contribute to the Breit–Pauli energy correction. Moreover, the geometrical derivatives of the molecular integrals in gradient calculations represent the perturbed operator and must be replaced by the Breit–Pauli integrals of Sec. IID to obtain the first-order energy correction. With these modifications, the first-order Breit–Pauli energy may be straightforwardly calculated with a gradient code.

The only problem that arises with the adaptation of the gradient code of Ref. 15 to the calculation of first-order relativistic corrections is related to the permutational symmetries of the orbit–orbit integrals, which are different from those assumed in the CCSD(T) gradient code. Following the discussion of Sec. III C in Ref. 15, the contraction of the triples density matrix elements  $d_{abc}^{(T)}$  and  $d_{abci}^{(T)}$  with two-electron integrals  $g_{abc}$  that are either symmetric or antisymmetric with respect to permutations of the last indices  $i$  and  $c$  may be carried out as

$$\sum_{abc} (d_{abc}^{(T)} g_{abc} + d_{abci}^{(T)} g_{abci}) = \sum_{abc} {}^S d_{abc}^{(T)} g_{abc}, \quad (78)$$

$${}^S d_{abc}^{(T)} = d_{abc}^{(T)} \pm d_{abci}^{(T)},$$

where  $a$ ,  $b$ , and  $c$  denote here virtual MOs and  $i$  occupied MOs. For the efficient calculation of properties, the symmetrized density elements  ${}^S d_{abc}^{(T)}$  are added to the effective density elements  $d_{abc}^{\text{eff}}$ . The plus sign in Eq. (78) is used whenever the contraction is made with integrals symmetric in the last two indices (as for molecular gradients in Ref. 15), whereas the minus sign is used for the antisymmetric Breit orbit–orbit integrals. A similar modification must be made for the triples density matrix elements  $d_{ijka}^{(T)}$  and  $d_{ijk}^{(T)}$  where  $i$ ,  $j$ , and  $k$  denote occupied and  $a$  unoccupied MOs.

### III. RESULTS AND DISCUSSION

All calculations presented here have been carried out using a development version of the quantum-chemistry code DALTON,<sup>16</sup> and a modification of the coupled-cluster molecular-gradient implementation of Ref. 15 as discussed in Sec. IIE.

The results presented in Table I were discussed already in Sec. I. We note here that the first-order corrections are dominated by the one-electron mass-velocity and Darwin terms (the Cowan–Griffin model). The two-electron terms are individually much smaller (about 1%) but cancel to a smaller extent and contribute as much as 5% to the total first-order relativistic correction. Of all contributions, the orbit–orbit contribution is the smallest one, constituting less than 1% the total correction.

TABLE II. First-order Breit corrections (in  $mE_h$ ) for selected molecules.

Molecule <sup>a</sup>	Basis <sup>b</sup>		Hartree–Fock			CCSD(full)		
			$E^{SS}$	$E^{OO}$	$E^{Breit}$	$E^{SS}$	$E^{OO}$	$E^{Breit}$
C <sub>2</sub> H <sub>6</sub>	u-cc-pCVDZ	This work	5.312	0.357	5.670	4.855	0.150	5.005
		Reference 4	5.312		5.672 <sup>c</sup>	4.85 <sup>d</sup>		
NH <sub>3</sub>	u-cc-pCVTZ	This work	4.397	0.392	4.789	4.002	0.209	4.211
		Reference 4	4.396		4.792 <sup>c</sup>	4.00 <sup>d</sup>		
H <sub>2</sub> O	u-cc-pCVTZ	This work	6.809	0.766	7.575	6.283	0.511	6.793
		Reference 4	6.810		7.582 <sup>c</sup>	6.28 <sup>d</sup>		
HCN	u-cc-pCVTZ	This work	7.051	0.529	7.580	6.388	0.232	6.620
		Reference 4	7.052		7.584 <sup>c</sup>	6.38 <sup>d</sup>		
HNCC	u-cc-pCVDZ	This work	13.831	1.292	15.123	12.881	0.854	13.735
		Reference 4	13.832		15.134 <sup>c</sup>	12.88 <sup>d</sup>		
HCOOH	u-cc-pCVDZ	This work	16.247	1.661	17.909	15.188	1.164	16.352
		Reference 4	16.248		17.924 <sup>c</sup>	15.18 <sup>d</sup>		
SiH <sub>3</sub> <sup>-</sup>	CVDZ	This work	43.771	10.941	54.711	42.078	10.081	52.159
		Reference 4	43.770		54.859 <sup>c</sup>	42.07 <sup>d</sup>		
SiC <sub>2</sub>	CVDZ	This work	49.084	11.193	60.277	46.953	10.138	57.091
		Reference 4	49.084		60.427 <sup>c</sup>	46.95 <sup>d</sup>		
H <sub>2</sub> S	CVDZ	This work	68.230	19.100	87.330	65.958	17.843	83.801
		Reference 4	68.230		87.639 <sup>c</sup>	65.95 <sup>d</sup>		

<sup>a</sup>Calculated equilibrium geometries taken from Ref. 4.

<sup>b</sup>See Ref. 4.

<sup>c</sup>Dirac–Hartree–Fock–Coulomb–Breit results obtained with the *Bertha* program.

<sup>d</sup>First-order CCSD(T)(full) value.

In Table II, we have listed the first-order Breit corrections to the total energy for the same molecules that were studied in Ref. 4, using the same basis sets and geometries. At the Hartree–Fock level of theory, it is possible to compare with Dirac–Hartree–Fock results. The agreement is in all cases excellent. Moreover, the small difference between the two methods is very systematic, depending in a simple manner on the types of atoms in the molecules, for example, each carbon, nitrogen, and oxygen atom contributes about 1, 3, and  $7\mu E_h$ , respectively, to the overall difference; for the heavier Si atom, the contribution is larger (about  $0.15mE_h$  per atom). We also note that, in all cases, the first-order Breit–Pauli treatment gives a too small relativistic correction to the energy. Comparing the Hartree–Fock and all-electron CCSD results, we find that correlation reduces the Breit correction, by 5%–10% (less for the heavier systems).

From Table II, we see that the first-order two-electron relativistic correction is dominated by the spin–spin interaction, the orbit–orbit interaction contributing only about 10% to the total Breit correction in molecules consisting of light atoms. However, the orbit–orbit term becomes relatively more important with increasing nuclear charges: in H<sub>2</sub>S, for example, it constitutes more than 20% of the total Breit cor-

rection. Both the spin–spin and orbit–orbit contributions are in all cases positive, increasing the total electronic energy.

In Table III, we compare the first-order Breit corrections obtained at the CCSD level of theory by correlating all electrons with those obtained by correlating only the valence electrons. Not surprisingly, most of the correlation correction to the Breit term occurs in the core.

#### IV. CONCLUSIONS

We have presented the first implementation of all terms that contribute to the first-order relativistic correction to the total electronic energy in molecular systems, including the two-electron orbit–orbit Breit interaction. Calculations including all first-order terms have been presented for a series of small and light molecules, at the Hartree–Fock and coupled-cluster levels of theory. By comparing with four-component Dirac–Coulomb–Breit calculations, we have demonstrated that the full Breit–Pauli energy corrections represent an accurate approximation to a fully relativistic treatment of such systems. The two-electron interactions are dominated by the spin–spin interaction, the orbit–orbit interaction contributing only about 10% to the Breit correction in

TABLE III. First-order Breit corrections (in  $mE_h$ ) for the Ne atom in the cc-pCVQZ basis.

Method	Frozen core			Correlated core		
	$E^{SS}$	$E^{OO}$	$E^{Breit}$	$E^{SS}$	$E^{OO}$	$E^{Breit}$
Hartree–Fock	14.234	2.384	16.618	14.234	2.384	16.618
MP2	14.075	2.282	16.357	13.197	1.865	15.062
CCSD	14.084	2.295	16.379	13.208	1.881	15.089
CCSD(T)	14.071	2.275	16.347	13.183	1.837	15.021

molecules consisting of light atoms. The importance of the orbit-orbit interaction increases somewhat with increasing nuclear charge, contributing more than 20% in H<sub>2</sub>S. The first-order Breit correction underestimates the infinite-order Breit correction slightly, each atom contributing a fixed amount (i.e., an amount independent of the molecular environment) to the error relative to the infinite-order treatment.

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