

INVITED PAPER

Anatomy of relativistic energy corrections in light molecular systems

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(Received 3 June 2001; accepted 11 June 2001)

Relativistic energy corrections which arise from the use of the Dirac–Coulomb Hamiltonian, and the Gaunt and Breit interaction operators, plus Lamb-shift effects have been determined for the global minima of the ground electronic states of C₂H₆, NH₃, H₂O, [H,C,N], HNCO, HCOOH, SiC₂, SiH₃⁻, and H₂S, and for barrier characteristics for these molecular systems (inversion barrier of NH₃ and SiH₃⁻, barrier to linearity of H₂O, H₂S, and HNCO, rotational barrier of C₂H₆, difference between conformations of HCOOH (*Z/E*) and SiC₂ (linear/T-shaped), and isomerization barrier of HCN/HNC). The relativistic calculations performed at the Hartree–Fock and the highly correlated CCSD(T) levels employed a wide variety of basis sets. Comparison of the perturbational and the four-component fully variational results indicate that the Coulomb–Pauli Hamiltonian and the lowest order Hamiltonian of direct perturbation theory (DPT(2)) are highly successful for treating the relativistic energy effects in light molecular systems both at a single point on the potential energy hypersurface and along the surface. Electron correlation contributions to the relativistic corrections are relatively small for the systems studied, and are comparable with the 2-electron Darwin correction. Corrections beyond the Dirac–Coulomb treatment are usually rather small, but may become important for high accuracy *ab initio* calculations.

1. Introduction

The chemical and physical consequences of relativistic phenomena are striking for elements in the lower part of the periodic table and, consequently, for their compounds [1–10]. In certain cases, the neglect of relativistic effects can lead to predictions of experimental observables which are qualitatively incorrect. Relevant examples include the ionization potential and the colour of gold, the liquid state of mercury, and the chemical properties of lanthanides and actinides, plus compounds involving these elements. The foundation of relativistic electronic structure theory, and the numerical results of relativistic computations on molecules containing heavy elements have been reviewed extensively by many workers in the field, including Pyykkö [1, 2, 8], Balasubramanian [3, 4] and Grant and Quiney [9].

The precision of non-relativistic quantum chemical treatments of light molecular systems now approaches the level [11–18] where the remaining errors in the electronic energies (see figure 1), at least in a relative sense, are negligible. As an example, it is perhaps sufficient to cite here our own recent *ab initio* results for the potential energy hypersurfaces (PESs) of H₃⁺ [15], H₂O [18] and H₂S [18, 19]. Therefore, one needs to worry about small correction terms to the electronic energies which are tacitly neglected in most quantum treatments on Born–Oppenheimer potential energy hypersurfaces (BO-PESs) [16], notably the relativistic, adiabatic and non-adiabatic corrections. The treatment of non-adiabatic corrections remains problematical [20]. The widely studied first-order adiabatic correction, called the diagonal Born–Oppenheimer correction (DBOC) [21–24] scales as Z^2/M , where Z is the atomic number and M is the molecular mass, and is especially important for the lightest systems. For chemically more interesting but still low Z systems, the relativistic effects, which

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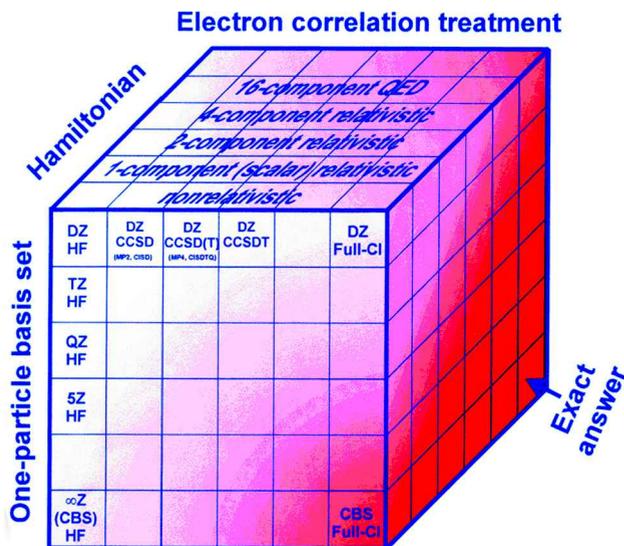


Figure 1. The magic cube of electronic structure theory showing, along the three axes, the three most important inherent approximations during solution of the time-independent Schrödinger equation within the Born–Oppenheimer approximation.

scale as $Z^4\alpha^2$, where α is the fine-structure constant, dominate. In this study a systematic investigation of relativistic effects is made, with special emphasis on the PESs of light molecular systems modelled by barriers [14].

The electronic states of some of the lightest one- to five-electron atomic and molecular systems have been investigated thoroughly by several techniques based on relativistic quantum mechanics [25–28]. These computations have proved to be extremely useful in assessing the applicability and utility of different relativistic formulations. A particularly impressive result is the construction of a highly accurate adiabatic PES of H_3^+ that includes relativistic effects [28]. To our knowledge there are only relatively few computations [29–34] of relativistic corrections to the electronic energy of molecular systems containing only light atoms of more chemical relevance than hydrogen. The important conclusions to be drawn from these studies, some of which have been emphasized in early relativistic works of Davidson and coworkers [29, 31, 33, 34] are as follows: (a) ‘almost all of the relativistic [energy] correction is associated with the core orbitals’ [31]; (b) nevertheless, almost all of the differential relativistic effect, involving the change of the relativistic energy correction over a PES, ‘is associated with [changes in] the valence shell’ [32]; (c) relativistic energy corrections obtained from first-order perturbation theory (which forms a central part of this study, see below) agree well with those from

Dirac–Hartree–Fock (DHF) calculations; (d) ‘for all atoms lighter than neon, and perhaps up to argon, first-order corrections [are] adequate for understanding relativistic corrections to the energies of molecules [34]; (e) the geometry dependence of relativistic effects is small [33]; and (f) relativistic corrections to PESs [18, 19, 35, 36] are larger than corrections due to some other physically relevant corrections, like DBOC. While examining several electronic states of formaldehyde, Phillips and Davidson [33] also observed that ‘[the] difference between the relativistic corrections for the free atoms and for the 1A_1 state of H_2CO is not due to modification of the 1s orbitals of oxygen or carbon [but that] there is a definitive correlation between the oxygen 2s population and the relativistic correction’. In the case of the ground electronic state of water [36] it was shown that relativistic corrections along the surface result in changes in vibrational band origins (VBOs) of approximately 0.1% in magnitude, which represents a substantial quantity of energy for higher lying states. In the most sophisticated model chemistries parts of the relativistic effects have been considered during accurate computation of total atomization energies [37–39].

Numerous methods exist which allow determination of relativistic corrections to computed energies and properties. The essential differences between these methods involve the choice of a ‘proper’ relativistic Hamiltonian, and the algebraic approach used to evaluate its eigenvalues. The most rigorous approaches construct a formulation from the fundamental principles embodied in quantum electrodynamics (QED) [40], but such calculations have been carried out for only few-electron systems, and to finite order in QED perturbation theory [10]. Recently, approximate non-relativistic and phenomenological treatments of the leading QED contribution, the Lamb shift (including vacuum-polarization (VP) and self-energy (SE) corrections), have been applied to model these effects in light molecular systems [41, 42].

The form that we might expect a ‘proper’ relativistic Hamiltonian to take remains, however, clouded in unresolved difficulties. These arise because of a fundamental incompatibility between the Hamiltonian, which asserts the conservation of energy of the system with respect to a *single* time parameter, and the special theory of relativity, which rejects absolute frames of reference and absolute time in favour of relative time intervals. These problems propagate through the formulation, introducing retarded interactions between particles, the creation of virtual electron–positron pairs, the frame dependence on the number and nature of the particles present in the system and, ultimately, the construction of divergent radiative quantities requiring the

renormalization of the mass and charge of electrons. The order-by-order prescription of Feynman diagrams, which define the structure of modern QED, betrays the essentially perturbative nature of relativistic quantum field theory. Whenever we adopt an apparently variational computational approach to the determination of many-electron relativistic atomic and molecular structures, therefore, it has to be remembered that we are actually solving a simplified physical model in a particular frame of reference whose validity is justified only by its success in reproducing experimental observations. No wholly satisfactory relativistic Hamiltonian quantum theory is available to us, and relativistic Lagrangian quantum theory leads naturally to order-by-order expansions characterized by the number of fundamental interactions involved at each order.

The most rigorous relativistic theories that can be applied more or less routinely to chemically interesting many-electron systems include variational four-component spinor methods, based on Dirac–Coulomb or Dirac–Coulomb–Gaunt/Breit/Brown [1, 9, 43, 44] Hamiltonians in the clamped nucleus approximation. In recent years, efficient computational procedures and programs have been developed, based on relativistic Dirac–Hartree–Fock (DHF) theory [45–48], density functional theory [49–51], many-body perturbation theory [52], configuration interaction [53], coupled cluster theory [26, 54] and semiempirical techniques [55–59]. Even though techniques such as kinetic balance [9] have been developed to avoid variational collapse [60, 61] of finite matrix solutions of the Dirac equation, and the theory has been placed on firm foundations by the resolution of difficulties associated with the continuum dissolution (also called Brown–Ravenhall disease [62–64] of the many-particle states constructed from four-spinors, the computational cost of four-component variational methods still limits their widespread use.

More simplified approaches have been explored which are based on perturbation theories applied to two- or one-component (non-relativistic) wavefunctions, using transformed, approximate quasi-relativistic Hamiltonians [65–84]. Although the perturbative treatment of relativistic effects requires little modification of existing non-relativistic codes, and the computational cost is significantly lower than the cost of four-component relativistic methods, perturbative approaches have not proved to be particularly popular. The main arguments against the use of perturbative techniques have been that (a) they contain singular operators and (b) the resulting perturbation series is either slowly convergent, or it is divergent. Due mostly to work by Kutzelnigg, it has become clear that the first counterargument is valid only for perturbation treatments based on the Foldy–Wouthuysen (FW) transformation [4, 65], like the mass–

velocity–Darwin (MVD) perturbation theory [66–68], or related approaches. These divergences, however, can be avoided. Relevant procedures include the direct perturbation theory (DPT) of Kutzelnigg [69–74] and others [75–77], perturbation theories based on Chang–Pélissier–Durand (CPD) [78] or Douglas–Kroll-transformed Hamiltonians [63, 79–82], or a combination of these approaches, like the *n*ORA techniques (e.g. the zero-order regular approximation, ZORA [83, 84]). The second argument becomes of practical importance only in the case of heavy elements [72], although of course the use of a divergent series may undermine the use of approximations which are based on assumptions regarding the ‘smallness’ of correction terms relative to the dominant non-relativistic structure. These observations, numerous numerical studies, and the fact that the Dirac–Coulomb–Gaunt/Breit/Brown Hamiltonian contains all physical terms only up to $O(Z^2\alpha^2)$, underpin the assumptions regarding the presumed adequacy of one- or two-component calculations for low *Z* molecular systems.

Finally, there exist simple methods that account for relativistic effects through the use of relativistic effective core potentials (RECPs) [1, 2, 4]. Because modification of non-relativistic codes required for handling RECPs is straightforward and the computational cost to use them is low, RECPs are widely employed in studies of heavy element chemistry, and particularly in theoretical investigations of transition metal compounds. Examination of RECP techniques does not, however, form part of this article.

The present paper has several purposes. (a) Accurate relativistic energy corrections are determined for prototypical light molecules; C_2H_6 , NH_3 , H_2O , $[H,C,N]$, $HNCO$, $HCOOH$, SiH_3^- , SiC_2 , and H_2S . These systems are of particular interest since their (dynamic) structure and related spectra have been the focus of several detailed experimental and theoretical studies, pushing *ab initio* techniques to their current technical limits [11, 12, 14, 16, 18, 85, 86]. (b) As a small but significant step towards determination of the effect of relativistic corrections on full PESSs, the contribution of relativistic effects to inversion barriers (NH_3 and SiH_3^-), rotational barriers (C_2H_6), barriers to linearity (H_2O , H_2S , and $HNCO$), conformational energy differences ($HCOOH$, SiC_2), and isomerization barriers ($[H,C,N]$ system) are investigated. (c) In order to gain further insight into the nature of the scalar relativistic terms of the (first-order) Pauli–Coulomb Hamiltonian, the one-electron mass–velocity (MV), and the one- and two-electron Darwin (D1 and D2, respectively) terms, together with the scalar contribution of the spin–own-orbit splitting are investigated separately; in particular, the D1 term is decomposed into atomic contributions. (d) The performance of

the MVD approximation is compared with the more accurate lowest order DPT theory. (e) The accuracy of perturbation theory results is checked against four-component variational calculations. (f) Further, smaller correction terms, the Gaunt, the Breit, and the Lamb-shift effects are evaluated. (g) Finally, where appropriate, basis set effects and the contribution of the electron correlation to the various relativistic terms are investigated.

2. Computational armamentarium

Reference structures for the relativistic computations have been determined, when not noted otherwise, at the all-electron, non-relativistic aug-cc-pVTZ CCSD(T) level. These non-relativistic geometries deviate only marginally from their relativistic counterparts. (The deviation of the non-relativistic (bond lengths/bond angles) from the corresponding relativistic ones is about (0.000 03 Å/0.07°) for H₂O [87] and (0.000 15 Å/0.9°) for H₂S [87]). The structural parameters employed are summarized in table 1. In the case of the isomerization reaction of the [H,C,N] system, the structure of the isomerization barrier was taken from [88], where it was determined at the cc-pCV5Z CCSD(T) level. The two reference structures of H₂S were taken from [12], and were obtained at the aug-cc-pVQZ CCSD(T) level.

The scalar mass–velocity (MV) and the one- and two-electron Darwin (D1 and D2, respectively) terms have been determined with a modified version of the DIRCC12 program system [101], upgraded for relativistic calculations according to the recipe of Klopper [102]. The relativistic corrections have been obtained by finite differences. Some of the one-electron mass–velocity and Darwin terms have been checked against results obtained analytically by the ACESII program [103]. Direct perturbation theory (DPT) has been applied at its lowest order using a modified version of Dalton (in the current implementation the spin part of the DPT(2) Hamiltonian has been neglected; the justification of this is demonstrated in § 3.4) [104]. The necessary computations have been carried out at the RHF and CCSD(T) levels of theory employing the correlation-consistent cc-pVXZ and cc-pCVXZ basis sets of Dunning and coworkers [105, 106], plus the uncontracted versions of the cc-pCVXZ basis sets, denoted as u-cc-pCVXZ in this study. Since cc-pCVXZ basis sets for second-row elements were not available for us, they were constructed [107] as follows for S and Si: the cc-pVXZ basis sets have been completely uncontracted and then augmented with tight (2d, 2f) sets, whose exponents were obtained by an even-tempered extension into the core with a geometric ratio of 3.0. The resulting basis sets are denoted as

CVXZ. In calculations employing the CVXZ basis sets, for all the other atoms the u-cc-pCVXZ sets have been used. Only the spherical harmonic components of the basis functions have been used. In electronic structure calculations including correlation effects, all electrons have been correlated.

The four-component variational calculations have been carried out at the Dirac–Hartree–Fock level using the MolDir [108] and Bertha [109, 110] program packages. The calculations employed spinor basis sets, to which the kinetic balance [9, 108b] prescription has been applied in order to generate the small component basis functions from the elements of the large component set. The variational relativistic corrections have been obtained as the difference between calculations using the speed of light $c = 137.035\,989\,5$ au and $c = 10\,000.0$ au. The Gaussian nuclear charge distribution model was used throughout, with the exponent factors recommended by the ‘REHE’ community [111]. Marginal deviations (e.g. about (30,340) μE_h for the total energy of (H₂O, H₂S) and less than (0.1, 0.1) cm^{-1} for the barriers to linearity) between the Gaussian distribution and the point-charge models were neglected when variational results are compared to one- and two-component perturbational (i.e. MVD and DPT) ones. Gaunt and Breit energy corrections have been determined perturbationally by the MolDir and Bertha packages, respectively, using four-component relativistic Dirac–Hartree–Fock wavefunctions. The difference between the perturbationally obtained Gaunt/Breit energy and the fully variational Dirac–Hartree–Fock–Gaunt/Breit result is minuscule, for example, it is $1.89 \mu E_h$ at the equilibrium structure of water, and 0.001cm^{-1} to the barrier to linearity of water.

The higher order scalar contribution of spin–own-orbit splitting (see below) has been determined as the difference of the results obtained by using the full four-component Dirac–Coulomb Hamiltonian and the four-component spin-free Dirac–Coulomb Hamiltonian of Dyall [112]. The latter Hamiltonian has recently been implemented in the Dirac 3.2.1 [113] program package. These calculations employed the Cartesian form of the uncontracted (u-cc-pCVXZ and CVXZ) basis sets of each element, except for the H basis, which was augmented by two tight p functions (with exponents 3 and 9 times the tightest existing p function exponent). This augmentation of the basis has been suggested in order to reduce the error made in the 2p spin–own-orbit splitting [114].

One- and two-electron Lamb-shift corrections have been obtained from renormalized one- and two-electron Darwin terms, respectively, using the recipe and the $R_{L/D}$ factors obtained in [42].

Table 1. Geometric parameters of the reference structures of the species investigated in this study.^a

Species	Parameter	Reference structure 1 (Equilibrium)		Reference structure 2 (Barrier)	
		Calculated ^b	Experimental ^c	Calculated ^b	Experimental ^c
NH ₃	$r(\text{N—H})$	1.011 98	1.013 8	0.995 19	
	$\alpha(\text{H—N—H})$	106.686	107.1	120.000	
H ₂ O	$r(\text{H—O})$	0.958 85	0.957 81(3)	0.934 11	0.9335 ^d
	$\alpha(\text{H—O—H})$	104.343	104.477 6(19)	180.000	180.000
HNCO	$r(\text{N—H})$	1.002 66	0.994 6(64)	0.984 73	
	$r(\text{N=C})$	1.216 49	1.214 0(24)	1.179 37	
	$r(\text{C=O})$	1.166 83	1.666 4(8)	1.176 80	
	$\alpha(\text{H—N=C})$	123.130	123.9(17)	180.00	
	$\alpha(\text{N=C=O})$	172.270	172.6(27)	180.00	
	$\phi(\text{H—N=C=O})$	180.00	180.00	180.00	
HCN/HNC	$r(\text{H—C})$	1.060 38/–	1.062 55(26)/–	1.183 5	
	$r(\text{H—N})$	–/0.995 09	–/0.994 0(8)	1.387 5	
	$r(\text{C—N})$	1.155 70/	1.168 92(2)/	1.186 7	
		1.171 41	1.152 87(7)		
H ₂ S	$r(\text{H—S})$	1.337 30	1.335 6(30)	1.315 93	
	$\alpha(\text{H—S—H})$	92.295	92.11(30)	180.000	
SiC ₂	$r(\text{Si—C})$	1.853 40	1.832 32(58)	1.705 70	
	$r(\text{C—C}')$	1.279 80	1.268 55(36)	1.292 00	
	$r(\text{Si—C}')$	1.853 40	1.832 32(58)	2.997 70	
SiH ₃ [–]	$r(\text{Si—H})$	1.537 53		1.476 41	
	$\alpha(\text{H—Si—H})$	95.196		120.000	
C ₂ H ₆	$r(\text{C—H})$	1.088 15	1.094 0(2)	1.087 08	
	$r(\text{C—C})$	1.522 99	1.535 1(1)	1.537 26	
	$\alpha(\text{C—C—H})$	111.128	111.17(1)	111.576	
	$\phi(\text{H—C—C—H})$	180.000	(180.000)	0.000	
HCOOH	$r(\text{C—H})$	1.095 46	1.105 0(43)	1.089 13	1.091(5)
	$r(\text{C=O})$	1.192 69	1.194 5(31)	1.199 06	1.201(5)
	$r(\text{C—O})$	1.348 98	1.352 0(28)	1.342 66	1.340(5)
	$r(\text{O—H})$	0.961 63	0.955 5(53)	0.966 95	0.969(5)
	$\alpha(\text{O—C=O})$	122.629	122.12(37)	125.057	124.80(50)
	$\alpha(\text{C—O—H})$	108.580	109.68(44)	106.320	106.61(50)
	$\alpha(\text{H—C=O})$	123.892	123.23(58)	125.141	123.26(50)

^a Bond lengths r in Å, bond angles α and dihedral angles ϕ in deg. For all species reference structure 1 corresponds to the global minimum on the ground electronic states PES, while reference structure 2 corresponds to the appropriate barrier (see text). In the case of HCOOH, reference structure 1 is the *Z* conformer, reference structure 2 is the *E* conformer.

^b The geometries of HCN, HNC, H₂O and NH₃ have been optimized at the unfrozen-core aug-cc-pVTZ CCSD(T) level. The geometries of HNCO, C₂H₆, and HCOOH have been optimized at the unfrozen-core cc-pVTZ CCSD(T) level of theory. The transition structure of the HCN–HNC inversion reaction is taken from [88]. The reference structures of H₂S are taken from [12].

^c Experimental structural parameters: HNCO, r_s structure [89]; HCN, r_c^* structure calculated from B_c^* , obtained by combining *ab initio* rovibrational (α) constants with experimental [90, 91]; HNC, r_c structure [90, 92]; H₂O, r_c structure [93]; H₂S, r_c structure [94]; SiC₂, r_s structure [95]; NH₃, r_s structure [96]; C₂H₆, r_z structure [97]; HCOOH, r_s structure (*E* [98] and *Z* [99]).

^d Obtained from the experimentally corrected *ab initio* PES of Partridge and Schwenke [100].

3. Relativistic Hamiltonians

3.1. Many-electron Hamiltonians

Starting from quantum-electrodynamics (QED) the effects not considered in non-relativistic electronic structure theory can be separated into three distinct contributions: (a) one-body effects arising directly and indirectly from the high velocity of the electrons; (b) two-body effects arising through the exchange of

virtual photons between charged particles (electrons); and (c) radiative corrections involving emission of virtual photons by a charged particle (electron) and subsequent reabsorption of the photon by the same particle.

The first of these contributions may be treated exactly by the use of the time-independent Dirac equation, which for one-electron systems is given by

$$h^D\psi = \left[c\alpha\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right) - eV + \beta mc^2 \right] \psi = E\psi, \quad (1)$$

where m , e , c , \mathbf{A} , α , \mathbf{p} , and β are defined according to the usual conventions [1]. In common with the well known approaches of non-relativistic theory, this equation can be generalized for many-electron systems by choosing an appropriate zero-order potential V to describe the electron–electron interaction. The simplest relativistic many-electron Hamiltonian can be defined by adding the Coulomb operator to h^D , resulting in the Dirac–Coulomb Hamiltonian

$$H^{DC} = \sum_i h_i^D + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}}. \quad (2)$$

We shall assume that this unquantized operator is employed initially only in order to generate a one-electron spectrum, and that the subsequent use of these four-spinors and of the Dirac–Coulomb operator is properly interpreted within a second-quantized formalism. These qualifications are essential if we are to avoid the problems described by Brown and Ravenhall [62] concerning the dissolution of many-electron bound states into the continuum.

This theory results in non-relativistic energies corrected by the so-called kinetic relativistic effects, which arise due to the high velocity of the electrons. A complete set of states is generated of both positive and negative energy character, and the interpretation of the model requires that we regard the few lowest positive-energy solutions as the single-particle bound states. The negative energy states are regarded in the first approximation as comprising a chemically inert core, whose (infinite) energy is removed on the grounds that it is unobservable.

Since the Coulomb term of the Dirac–Coulomb Hamiltonian is not a Lorentz-invariant quantity, the next level of sophistication after the evaluation of the kinetic relativistic effects demands consideration of the effect of special relativity on the form of the interelectron potential. In the first order of perturbation theory this can be achieved by ‘switching’ from the Coulomb potential to the quasi-Lorentz-invariant Gaunt or Breit (or the more sophisticated Brown) potential. (Because these potentials can be derived from QED [10] as well as semiclassically [44], some authors consider them as QED effects, while others define only terms beyond these as QED effects.) The Gaunt and Breit potentials are defined as [43–45]

$$V_{ij}^{\text{Gaunt}} = \frac{1}{r_{ij}} - \frac{\alpha_i \alpha_j}{r_{ij}} \quad (3)$$

and

$$V_{ij}^{\text{Breit}} = \frac{1}{r_{ij}} - \frac{1}{2} \left(\frac{\alpha_i \alpha_j}{r_{ij}} + \frac{(\alpha_i \mathbf{r}_{ij})(\alpha_j \mathbf{r}_{ij})}{r_{ij}^3} \right). \quad (4)$$

The first term of the Gaunt potential, V^{Gaunt} , is the usual Coulomb operator, the second term is a magnetic interaction. The difference between the Gaunt and Breit operators provides a low energy approximation of the effects of retardation on the interaction, and sometimes is referred to as a gauge term, because its form depends on the radiation gauge which is selected.

A fully Lorentz-invariant description requires consideration of the third contribution, which involves the explicit renormalization of the mass and charge of the electron. The emission of virtual photons by a charged particle (electron) and reabsorption by the same particle, the so-called self-interaction, together with the vacuum polarization form the leading part of the Lamb-shift effect. A simple treatment to obtain the leading Lamb-shift effects, involving rescaling of the Darwin terms, has been outlined in [41, 42].

3.2. The Pauli Hamiltonians

As mentioned in § 1, transformation of the four-component equations results in approximations of two-component form. One of these approximations is the (first-order) Pauli Hamiltonian, which can be obtained by FW transformation [4, 65]. This is the best known approach and the easiest to plug into a non-relativistic electronic structure program. Since its constituent terms can be given simple interpretations by physical arguments, we discuss briefly the Pauli Hamiltonians obtained by reduction of the available four-component Hamiltonians.

We start from the Dirac–Coulomb–Breit Hamiltonian. In the absence of an external field, and neglecting the various interactions of the electrons with the spins of the nuclei, and among the spins of the nuclei, the following terms can be deduced [1, 4, 87]:

$$H_0 = - \sum_i \frac{1}{2} \mathbf{p}_i^2 + \frac{1}{2} \sum_{i,j \neq i} \frac{1}{r_{ij}} - \sum_{i,K} \frac{Z_K}{r_{iK}} + \sum_{K,L} \frac{Z_K Z_L}{R_{KL}}, \quad (5a)$$

$$H^{\text{MV}} = - \frac{1}{8c^2} \sum_i \mathbf{p}_i^4, \quad (5b)$$

$$H^D = H^{D1} + H^{D2} = \frac{\pi}{2c^2} \sum_{i,K} Z_K \delta(r_{iK}) - \frac{\pi}{2c^2} \sum_{i,j \neq i} \delta(r_{ij}), \quad (5c)$$

$$H^{\text{SO}} = H^{\text{SO1}} + H^{\text{SO2}} = \frac{1}{2c^2} \sum_{i,K} Z_K \frac{\boldsymbol{\sigma}_i \cdot (\mathbf{r}_{iK} \times \mathbf{p}_i)}{r_{iK}^3} - \frac{1}{2c^2} \sum_{i,j \neq i} \frac{\boldsymbol{\sigma}_i \cdot (\mathbf{r}_{ij} \times \mathbf{p}_i)}{r_{ij}^3}, \quad (5d)$$

$$H^{\text{SoO}} = -\frac{1}{c^2} \sum_{i,j \neq i} \frac{\boldsymbol{\sigma}_i \cdot (\mathbf{r}_{ij} \times \mathbf{p}_j)}{r_{ij}^3}, \quad (5e)$$

$$H^{\text{SS}} = H^{\text{FC}} + H^{\text{DP}} = \frac{1}{2c^2} \left\{ -\frac{8\pi}{3} \sum_{i,j \neq i} (\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j) \delta(r_{ij}) + \sum_{i,j \neq i} \left(\frac{\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j}{r_{ij}^3} - 3 \frac{(\boldsymbol{\sigma}_i \cdot \mathbf{r}_{ij})(\mathbf{r}_{ij} \cdot \boldsymbol{\sigma}_j)}{r_{ij}^5} \right) \right\}, \quad (5f)$$

$$H^{\text{OO}} = \frac{1}{4c^2} \sum_{i,j \neq i} \left(\frac{\mathbf{p}_i \cdot \mathbf{p}_j}{r_{ij}} + \frac{(\mathbf{p}_i \cdot \mathbf{r}_{ij})(\mathbf{r}_{ij} \cdot \mathbf{p}_j)}{r_{ij}^3} \right), \quad (5g)$$

where the indices i and j run over the electrons, while the indices K and L stand for the nuclei. Among these terms H_0 is the usual non-relativistic, clamped-nuclei Hamiltonian, the other terms are the mass-velocity (H^{MV}), the Darwin (H^{D}), the spin-own-orbit (H^{SO}), the spin-other-orbit (H^{SoO}), the spin-spin (H^{SS}), and the orbit-orbit (H^{OO}) Hamiltonians, respectively. As is also indicated above, H^{D} and H^{SO} can be further split into one- and two-electron contributions, while H^{SS} contains the Fermi-contact (H^{FC}) and the dipolar interaction (H^{DP}) terms.

Note that calculations based on these formulas include two approximations. First, the transformation included only the first-order term of a power series. Second, to avoid the singularities present in some of the operators usually the terms are evaluated by first-order perturbation theory using the eigenfunctions of H_0 . This so-called Breit–Pauli Hamiltonian can be simplified further by starting the FW transformation from the Dirac–Coulomb–Gaunt or the Dirac–Coulomb Hamiltonians. The Gaunt–Pauli Hamiltonian neglects the H^{OO} and H^{DP} terms of the Breit–Pauli Hamiltonian. Only the H_0 , the H^{MV} , the H^{D} , and the H^{SO} terms survive in the Coulomb–Pauli Hamiltonian. Further significant simplifications are obtained through the neglect of the non-scalar H^{SO} term, which results in a one-component theory, the so-called mass–velocity–Darwin (MVD2), or Cowan–Griffin perturbation theory [66]. Finally, in many computational studies even the $H^{\text{D}2}$ term is neglected, and only the one-electron scalar terms are considered (MVD1).

4. Relativistic corrections resulting from Dirac–Coulomb theory (kinetic relativistic corrections)

Numerical values obtained as part of this study for the various kinetic relativistic contributions are collected in tables 2–11. Data corresponding to the different molecules at the respective global minima of their ground electronic states, computed at the RHF and CCSD(T) levels employing basis sets of varying quality, are collected in tables 2, 4, 6, 8 and 10, while in tables 3, 5, 7, 9

and 11 the values corresponding to the differences in the various terms at two reference structures are shown, constituting part of the relativistic correction to the inversion barrier of NH_3 and SiH_3^- , the rotational barrier of C_2H_6 , the barrier to linearity of H_2O , H_2S , and HNCO , the conformational energy difference between HCN and HNC , Z - and E - HCOOH , and the T-shape and linear forms of SiC_2 .

4.1. The mass–velocity (MV) term

The physical significance of H^{MV} is that it serves to correct the kinetic energy of the electrons due to the variation of electron mass with velocity. The MV energy correction E^{MV} is always negative. The E^{MV} data obtained in this study are presented in tables 2 and 3. They reveal that the molecular E^{MV} values are, to a good degree of approximation, constructed additively from atomic values. The magnitude of the quasi-atomic terms increases as Z^4 , where Z is the full nuclear charge. This is in general agreement with the following elementary result for H-like systems:

$$E^{\text{MV}} = -\frac{\alpha^2 Z^4}{n^3} \left[\frac{1}{(l + \frac{1}{2})} - \frac{3}{4n} \right], \quad (6)$$

where n and l are the principal and angular momentum quantum numbers, respectively.

We are aware of only one previous study concerning the basis-set convergence of the MV terms in which Halkier *et al.* [115] showed for a limited number of cases using correlated wavefunctions that E^{MV} converges only slowly, approximately as X^{-1} , to the numerical results approximating the complete basis set (CBS) limit.

Based on the limited number of available data in the third and fourth columns of table 2, the convergence characteristics of the RHF and CCSD(T) values seem to be similar. However, this observation is deceptive, and is due to the fact that the correlation contribution to the MV term is small, of the order of only 0.1% of the total, as can be seen from the last column of table 2. The correlation increment to the E^{MV} values changes substantially, based on the quality of the basis set, the u-cc-pCVXZ and the cc-pCVXZ increments being much larger than the cc-pVXZ ones, suggesting the inferiority of the latter basis sets. However, the RHF E^{MV} terms seem to be much more sensitive to changes in the cardinal number (X) in the basis than to the augmentation of the basis set by core functions (+C); this is due to the fact that the cc-pV($X+1$)Z basis contains s functions with larger exponents than the corresponding cc-pCVXZ basis. To elaborate on this observation, we replaced the +C s function of the O-centred u-cc-pCVDZ basis with an s function having an exponent 3

Table 2. Mass-velocity (MV) energy corrections (E^{MV}/mE_h) and correlation energy contributions [$\delta(E^{MV})/\mu E_h$] to MV energies for selected molecules at their equilibrium structures.^a

Compound	Basis	E^{MV}		$\delta(E^{MV})^b$
		RHF	CCSD(T)	
C ₂ H ₆	cc-pVDZ(58)	-150.536	-150.532	
	cc-pCVDZ(66)	-150.298	-150.547	-249
	u-cc-pCVDZ(102)	-150.296	-150.593	-298
	cc-pVTZ(144)	-150.791	-150.749	
	cc-pCVTZ(170)	-150.852	-151.292	-440
NH ₃	cc-pVDZ(29)	-143.420	-143.426	
	cc-pCVDZ(33)	-143.341	-143.341	0
	u-cc-pCVDZ(51)	-143.326	-143.571	-245
	cc-pVTZ(72)	-143.883	-143.855	
	cc-pCVTZ(85)	-143.915	-144.255	-340
	u-cc-PVTZ(103)	-143.914	-144.189	-275
	cc-pVQZ(145)	-146.173	-146.297	
	cc-pCVQZ(174)	-146.175	-146.483	-308
H ₂ O	cc-pVDZ(24)	-250.429	-250.443	
	cc-pCVDZ(28)	-250.331	-250.632	-301
	u-cc-pCVDZ(44)	-250.347	-250.708	-361
	cc-pVTZ(58)	-251.454	-251.472	
	cc-pCVTZ(71)	-251.507	-252.002	-495
	u-cc-pCVTZ(87)	-251.524	-251.928	-404
	cc-pVQZ(115)	-255.429	-255.638	
	cc-pCVQZ(144)	-255.456	-255.903	-447
	cc-pV5Z(201)	-256.883	-257.136	
	cc-pCV5Z(255)	-256.862	-257.316	-454
	cc-pVDZ(33)	-219.761	-219.771	
HCN	cc-pCVDZ(41)	-219.561	-219.850	-289
	u-cc-pCVDZ(67)	-219.517	-219.875	-358
	cc-pVTZ(74)	-220.343	-220.220	
	cc-pCVTZ(100)	-220.354	-220.869	-515
	u-cc-pCVTZ(126)	-220.370	-220.782	-412
	cc-pVQZ(140)	-223.884	-224.019	
	cc-pCVQZ(198)	-223.891	-224.353	-462
	cc-V5Z(237)	-225.327	-225.555	
	cc-pVDZ(47)	-469.787	-469.781	
	cc-pCVDZ(59)	-469.540	-470.124	-584
	u-cc-pCVDZ(97)	-469.494	-470.213	-719
cc-pVTZ(104)	-471.355	-471.233		
cc-pCVTZ(143)	-471.473	-472.483	-1010	
cc-pVQZ(195)	-478.930	-479.285		
HCOOH	cc-pVDZ(52)	-576.608	-576.697	
	cc-pCVDZ(64)	-576.316	-577.125	-809
	u-cc-pCVDZ(104)	-576.314	-577.277	-963
	cc-pVTZ(118)	-578.575	-578.613	
	cc-pCVTZ(157)	-578.828	-580.106	-1278
SiH ₃ ⁻	cc-pVDZ(33)	-2606.71	-2606.73	
	CVDZ(72)	-2606.61	-2608.23	1620
	cc-pVTZ(76)	-2633.37	-2632.85	
	CVTZ(131)	-2633.22	-2634.58	1360
SiC ₂	cc-pVQZ(149)	-2643.32	-2642.93	
	cc-pVTZ(94)	-2787.59	-2786.51	
	CVDZ(111)	-2760.45	-2761.95	-1492
	cc-pVQZ(169)	-2799.91	-2799.25	
H ₂ S	CVRZ(193)	-2787.56	-2788.89	-1330
	cc-pVDZ(28)	-4548.99	-4549.02	
	cc-pVTZ(62)	-4594.61	-4594.12	
	CVDZ(65)	-4548.95	-4550.88	-1928

continued

Table 2. *Continued.*

Compound	Basis	E^{MV}		$\delta(E^{MV})^b$
		RHF	CCSD(T)	
	CVTZ(115)	−4594.49	−4596.12	−1634
	cc-pVQZ(119)	−4610.02	−4609.33	
	CVQZ(193)	−4609.84	−4611.51	−1668
	cc-pV5Z(205)	−4634.13	−4633.25	

^a The number of contracted Gaussian functions (CGFs) in a given basis set for a given molecule is indicated in parentheses. See text for description of the basis sets. Note that different computer programs will compute slightly different E^{MV} results when using cc-pVXZ basis sets. This problem is related to the different number of significant digits of the contraction coefficients when obtained from [106]. For example, using the cc-pV5Z basis for H₂S and the ACES II code [103] with the usual F10.7 format for the contraction coefficients results in −4634.287 and −4633.391 at the RHF and CCSD(T) levels, respectively (the corresponding $\delta(E^{MV})$ value is 896). The difference can be attributed to the tightest *s* function with exponent 5 481 000 of S (e.g. in the first contracted Gaussian the contraction coefficient is 19×10^{-7} vs 189×10^{-8}).

^b $\delta(E^{MV})$ values are given only for basis sets designed to describe core-valence correlation, such as (u)-cc-pCVXZ and CVXZ.

Table 3. Mass-velocity energy corrections ($\Delta E^{MV}/\text{cm}^{-1}$) and correlation energy contributions to ΔE^{MV} energies [$\delta(\Delta E^{MV})/\text{cm}^{-1}$] for barriers of selected compounds^a

Compound	Basis	ΔE^{MV}		$\delta(\Delta E^{MV})^b$
		RHF	CCSD(T)	
C ₂ H ₆ (eclipsed-staggered)	cc-pVDZ(58)	0.92	1.02	
	c-pCVDZ(66)	1.37	1.32	−0.05
	u-cc-pCVDZ(102)	1.47	1.37	−0.10
	cc-pVTZ(144)	2.66	3.76	
NH ₃ (planar-bent)	cc-pVDZ(29)	67.28	75.37	
	cc-pCVDZ(33)	88.09	92.12	4.03
	u-cc-pCVDZ(51)	88.60	92.98	4.38
	cc-pVTZ(72)	85.62	86.88	
	cc-pCVTZ(85)	82.85	84.75	1.90
	u-cc-pCVTZ(103)	82.18	83.60	1.42
	cc-pVQZ(145)	81.65	81.29	
	cc-pCVQZ(174)	80.56	80.51	−0.05
H ₂ O (linear-bent)	cc-pVDZ(24)	180.48	204.40	
	cc-pCVDZ(28)	225.49	238.67	13.18
	u-cc-pCVDZ(44)	230.09	244.42	14.33
	cc-pVTZ(58)	211.06	222.42	
	cc-pCVTZ(71)	211.78	219.51	7.73
	u-cc-pCVTZ(87)	214.44	221.34	6.90
	cc-pVQZ(115)	214.35	216.40	
	cc-pCVQZ(144)	211.82	215.21	3.39
	cc-pV5Z(201)	209.44	210.63	
	cc-pCV5Z(255)	209.73	211.28	1.55
[H,N,C] (HNC-HCN)	cc-pVDZ(33)	40.42	35.41	
	cc-pCVDZ(41)	61.23	51.14	−10.09
	u-cc-pCVDZ(67)	61.42	51.83	−9.59
	cc-pVTZ(74)	54.20	45.06	
	cc-pCVTZ(100)	59.27	49.06	−10.21
	u-cc-pCVTZ(126)	60.86	50.41	−10.45
	cc-pVQZ(140)	62.64	50.25	
	cc-pCVQZ(198)	60.87	50.07	−10.80
[H,N,C] (NHC (barrier)-HCN)	cc-pVDZ(33)	−97.12	−75.85	
	cc-pCVDZ(41)	−105.39	−85.58	19.81

continued

Table 3. *Continued.*

Compound	Basis	ΔE^{MV}		$\delta(\Delta E^{\text{MV}})^b$
		RHF	CCSD(T)	
HNCO (linear-bent)	u-cc-pCVDZ(67)	-107.69	-88.28	-19.41
	cc-pVTZ(74)	-112.61	-91.15	
	cc-pCVTZ(100)	-106.88	-87.94	18.94
	u-cc-pCVTZ(126)	-106.92	-87.36	19.56
	cc-pVQZ(140)	-108.50	-86.75	
	cc-pCVQZ(198)	-108.37	-88.96	19.41
	cc-pV5Z(237)	-109.01	-89.01	
	cc-pVDZ(47)	89.68	85.35	
	cc-pCVDZ(59)	117.20	108.66	-8.54
	u-cc-pCVDZ(97)	120.01	112.52	-7.49
HCOOH (<i>Z-E</i>)	cc-pVTZ(104)	123.78	112.98	
	cc-pCVTZ(143)	117.85	109.53	-8.32
	cc-pVQZ(195)	117.08	104.44	
	cc-pVDZ(52)	3.15	4.15	
	cc-pCVDZ(64)	1.70	3.81	2.11
	u-cc-pCVDZ(104)	1.27	3.49	2.22
SiH ₃ ⁻ (planar-bent)	cc-pVTZ(118)	0.34	1.62	
	cc-pCVTZ(157)	-0.07	1.87	1.93
	cc-pVDZ(33)	337.6	335.0	
	CVDZ(72)	392.2	405.4	13.2
	cc-pVTZ(76)	331.2	325.8	
SiC ₂ (linear-T-shaped)	CVTZ(131)	379.6	382.8	3.2
	cc-pVQZ(149)	281.5	286.0	
	cc-pVTZ(94)	-15.0	-63.3	
	CVDZ(111)	9.88	-34.24	-44.1
	cc-pVQZ(169)	-12.3	-54.5	
H ₂ S (linear-bent)	CVTZ(193)	5.05	-35.45	-40.5
	cc-pVDZ(28)	808.8	843.1	
	cc-pVTZ(62)	798.4	810.3	
	CVDZ(65)	908.2	962.5	54.3
	CVTZ(115)	888.4	906.4	18.0
	cc-pVQZ(119)	745.3	760.7	
	CVQZ(193)	883.3	891.7	8.5
	cc-pV5Z(205)	816.9	835.8	

See table 2 for footnotes.

times the exponent of the tightest *s* function of the cc-pVDZ basis. The resulting E^{MV} (RHF) values is $-252.908 mE_h$ for the equilibrium structure of water, substantially lower than the result obtained with the cc-pCVTZ basis set. Similar results were obtained for higher *X* sets. By contrast, the increase in observed correlation energy contribution to E^{MV} (RHF) with increasing *X* seems to be a real effect. Nevertheless, no clear basis set convergence can be seen for either the RHF energy or for the correlation contribution in any of the cases investigated in this study.

From table 3 it is clear that convergence characteristics of the ΔE^{MV} terms, where ΔE^{MV} is the mass-velocity energy correction to the barrier, is considerably

better than that observed for the E^{MV} values. The difference between the results obtained with cc-pVXZ and cc-pCVXZ basis sets is also much smaller in this case.

It is also interesting to note that for NH₃ and H₂O, where substantial sp rehybridization takes place between the two reference forms and therefore the largest total relativistic contributions to the barrier have been found among the molecules studied, $\delta(\Delta E^{\text{MV}})$, where $\delta(\Delta E^{\text{MV}})$ stands for the correlation energy contribution to the barrier, tends to become smaller and smaller as the basis set is expanded. Due to the slow convergence of the correlation contributions to ΔE^{MV} , it is very hard to establish apparent limits for $\delta(\Delta E^{\text{MV}})$. Nevertheless, assuming an X^{-1} dependence and using cc-pVXZ ener-

Table 4. Atomic ('atoms in molecules') one-electron Darwin energy corrections (E^{D1}/mE_h) to total energies of selected molecules at their equilibrium structures.

Method	Compound	Basis	H	C	N	O	Si	S	
RHF	C ₂ H ₆	cc-pVDZ(58)	0.032	60.545					
		cc-pCVDZ(66)	0.032	60.466					
		cc-pVTZ(144)	0.036	60.696					
	NH ₃	cc-pVDZ(29)	0.031			114.616			
		cc-pCVDZ(33)	0.031			114.550			
		cc-pVTZ(72)	0.035			115.045			
		cc-pCVTZ(85)	0.035			115.056			
		cc-pVQZ(145)	0.037			117.262			
		cc-pCVQZ(174)	0.037			117.257			
	H ₂ O	cc-pVDZ(24)	0.030				198.874		
		cc-pCVDZ(28)	0.030				198.787		
		cc-pVTZ(58)	0.034				198.808		
		cc-pCVTZ(72)	0.034				199.823		
		cc-pVQZ(115)	0.036				203.630		
		cc-pCVQZ(144)	0.035				203.617		
	HCN	cc-pV5Z(201)	0.037				205.067		
		cc-pVDZ(33)	0.030	60.791	115.229				
		cc-pCVDZ(41)	0.030	60.714	115.164				
		cc-pVTZ(74)	0.033	60.954	115.669				
		cc-pCVTZ(100)	0.033	60.964	115.658				
		cc-pVQZ(140)	0.034	62.171	117.886				
		cc-pCVQZ(198)	0.035	62.174	117.878				
		cc-pV5Z(237)	0.037	62.668	118.777				
	HNCO	cc-pVDZ(47)	0.029	60.743	114.718		199.183		
		cc-pCVDZ(59)	0.030	60.763	114.597		199.089		
		cc-pVTZ(104)	0.033	61.023	115.088		200.072		
		cc-pCVTZ(143)	0.033	61.020	115.094		200.110		
		cc-pVQZ(195)	0.034	62.225	117.305		203.937		
	HCOOH ^d	cc-pVDZ(52)	0.032/ 0.029	60.603			199.161/ 198.951		
		cc-pCVDZ(64)	0.032/ 0.029	60.605			199.037/ 198.845		
		cc-pVTZ(118)	0.036/ 0.033	60.852			200.016/ 199.811		
		cc-pVDZ(33)	0.028					2006.93	
	SiH ₃ ⁻	cc-pVTZ(76)	0.032					2032.76	
cc-pVTZ(94)				61.08			2034.74		
SiC ₂	cc-pVDZ(28)	0.028						3473.504	
	cc-pVTZ(62)	0.031						3517.802	
	cc-pVQZ(119)	0.033						3532.736	
	cc-pV5Z(205)	0.034						3556.727	
CCSD(T)	C ₂ H ₆	cc-pVDZ(58)	0.032	60.524					
		cc-pCVDZ(66)	0.032	60.472					
		cc-pVTZ(144)	0.036	60.631					
	NH ₃	cc-pVDZ(29)	0.032			114.588			
		cc-pCVDZ(33)	0.031			114.568			
		cc-VTZ(72)	0.036			114.946			
		cc-pCVTZ(85)	0.036			115.089			
		cc-pVQZ(145)	0.037			117.213			
	H ₂ O	cc-pCVQZ(174)	0.037			117.264			
		cc-pVDZ(24)	0.031				198.843		
		cc-pCVDZ(28)	0.031				198.829		
		cc-pVTZ(58)	0.035				199.696		
		cc-pCVTZ(71)	0.035				199.872		

continued

Table 4. *Continued.*

Method	Compound	Basis	H	C	N	O	Si	S
		cc-pVQZ(115)	0.036			203.573		
		cc-pCVQZ(144)	0.036			203.624		
		cc-pV5Z(201)	0.037			205.013		
	HCN	cc-pVDZ(33)	0.030	60.774	115.190			
		cc-pCVDZ(41)	0.030	60.717	115.153			
		cc-pVTZ(74)	0.034	60.875	115.537			
		cc-pCVTZ(100)	0.034	60.982	115.663			
		cc-pVQZ(140)	0.035	62.132	117.803			
		cc-pCVQZ(198)	0.035	62.174	117.857			
		cc-pV5Z(237)	0.037	62.641	118.708			
	HNCO	cc-pVDZ(47)	0.030	60.699	114.682	199.157		
		cc-pCVDZ(59)	0.030	60.719	114.616	199.144		
		cc-pVTZ(104)	0.033	60.894	114.992	199.964		
		cc-pCVTZ(143)	0.033	60.992	115.131	200.173		
	HCOOH ^a	cc-pVQZ(195)	0.035	62.136	117.261	203.897		
		cc-pVDZ(52)	0.032/ 0.030	60.586		199.138/ 198.951		
		cc-pCVDZ(64)	0.032/ 0.030	60.599		199.093/ 198.935		
		cc-pVTZ(118)	0.036/ 0.033	60.767		199.912/ 199.737		
		SiH ₃ ⁻	cc-pVDZ(33)	0.029				2006.96
		cc-pVTZ(76)	0.032				2032.58	
	SiC ₂	cc-pVTZ(94)		61.08			2034.74	
	H ₂ S	cc-pVDZ(28)	0.029					3473.56
		cc-pVTZ(62)	0.032					3517.67
		cc-pVQZ(119)	0.033					3532.45
		cc-pV5Z(205)	0.034					3555.68

^a The order of the H/H and O/O results corresponds to the order of the atoms in the structural formula. See footnote ^a in table 2.

gies with $X = 4$ and 5, the $\delta(\Delta E^{\text{MV}})$ limit of -1.32 cm^{-1} can be determined for water. The cc-pCVXZ energies with $X = 3$ and 4 result in a limiting value of -5.90 cm^{-1} for NH_3 . The closeness of these limits to zero is remarkable, especially in the light of the apparent nonzero limits that can be deduced for other molecular systems. The very different convergence characteristics of $\delta(\Delta E^{\text{MV}})$ in the case of H_2S should also be noted. Most of the time, extrapolation of either the E^{MV} or the ΔE^{MV} results cannot be performed due to the uneven convergence patterns observed in the respective energy values. Our limited numerical evidence seems to suggest that the excellent convergence characteristics of the correlation-consistent basis sets in non-relativistic energy calculations may not hold for relativistic energy calculations.

4.2. The one-electron Darwin (D1) term

The D1 term arises from the smearing of the electrons due to their high speed. It can be considered as a correction to the distance between the electrons and the nuclei

resulting in an overall decrease in the Coulomb attraction. Consequently, the D1 term always increases the total energy of the system. Since the sign of this term is opposite to that of the MV term and the magnitudes of E^{D1} and E^{MV} are similar, most of these effects are mutually cancelled. As can be seen from the equation for H^{D1} , the molecular D1 energy correction can be decomposed into individual atomic contributions. These atomic E^{D1} values of the molecules studied, computed again at the RHF and CCSD(T) levels and employing different basis sets, are collected in tables 4 and 5. One of the main advantages of this decomposition is the clear indication of the correlation between hybridization (s character of valence orbitals) and relativistic energy contributions upon change of molecular geometry. As an example, in the case of the barrier to linearity of HNCO, 65% of ΔE^{D1} originates from the N atom, whose hybridization changes the most between the two reference structures. Furthermore, this decomposition becomes important for the estimation of the Lamb-shift effect [41, 42], as discussed in detail in § 5.2.

Table 5. Atomic one-electron Darwin energy corrections ($\Delta E^{D1}/\text{cm}^{-1}$) to *barriers* of selected compounds.

Method	Compound	Basis	H	C	N	O	Si	S	
RHF	C ₂ H ₆	cc-pVDZ(58)	0.00	-0.31					
		cc-pCVDZ(66)	0.00	-0.44					
		cc-pVTZ(144)	0.01	-0.83					
	NH ₃	cc-pVDZ(29)	-0.13		-52.18				
		cc-pCVDZ(33)	-0.13		-64.68				
		cc-pVTZ(72)	-0.06		-62.92				
		cc-pCVTZ(85)	-0.06		-61.55				
		cc-pVQZ(145)	-0.07		-60.71				
		cc-pCVQZ(174)	-0.07		-60.27				
		H ₂ O	cc-pVDZ(24)	-0.78			-138.29		
	cc-pCVDZ(28)		-0.78			-165.25			
	cc-pVTZ(58)		-0.85			-156.56			
	cc-pCVTZ(71)		-0.85			-157.33			
	cc-pVQZ(115)		-0.87			-158.56			
	cc-pCVQZ(144)		-0.87			-157.55			
	cc-pV5Z(201)		-0.88			-156.17			
	[H,N,C] (HNC-HCN)	cc-pVDZ(33)	-0.26	64.07	-96.51				
		cc-pCVDZ(41)	-0.26	72.35	-117.03				
		cc-pVTZ(74)	-0.32	74.80	-116.68				
		cc-pCVTZ(100)	-0.32	71.05	-115.95				
		cc-pVQZ(140)	-0.34	72.16	-118.87				
		cc-pCVQZ(198)	-0.35	72.32	-118.32				
		cc-pV5Z(237)	-0.37	72.48	-118.61				
	[H,N,C] (NHC-HCN)	cc-pVDZ(33)	-1.21	43.44	28.16				
		cc-pCVDZ(41)	-1.22	47.32	29.44				
		cc-pVTZ(74)	-1.54	48.50	32.29				
		cc-pCVTZ(100)	-1.54	46.24	31.40				
		cc-pVQZ(140)	-1.66	46.90	32.27				
		cc-pCVQZ(198)	-1.66	47.16	32.06				
		cc-pV5Z(237)	-1.71	32.38	47.44				
	HNCO	cc-pVDZ(47)	-0.22	-15.63	-46.57	-7.27			
		cc-pCVDZ(59)	-0.21	-17.49	-60.27	-8.21			
		cc-pVTZ(104)	-0.25	-19.02	-59.42	-11.07			
		cc-pCVTZ(143)	-0.26	-17.90	-60.14	-8.52			
		cc-pVQZ(195)	-0.25	-18.01	-60.44	-8.28			
	HCOOH ^d	cc-pVDZ(52)	0.02/ 0.22	-2.06		1.20/ -1.71			
		cc-pCVDZ(64)	0.02/ 0.22	-2.06		2.06/ -1.43			
		cc-pVTZ(118)	-0.01/ 0.17	-2.11		1.81/ -2.95			
		SiH ₃ ⁻	cc-pVDZ(33)	-0.12				-254.71	
			cc-pVTZ(76)	-0.16				-255.03	
SiC ₂ ^b	cc-pVTZ(94)		-33.33/ 58.14			-22.46			
H ₂ S	cc-pVDZ(28)	-1.29					-606.33		
	cc-pVTZ(62)	-1.36					-615.31		
	cc-pVQZ(119)	-1.44					-585.64		
	cc-pV5Z(205)	-1.51					-626.17		
	CCSD(T)	C ₂ H ₆	cc-pVDZ(58)	0.00	-0.35				
cc-pCVDZ(66)			0.00	-0.43					
cc-pVTZ(144)			0.01	-1.09					
NH ₃		c-pVDZ(29)	-0.12		-57.13				
		cc-pCVDZ(33)	-0.12		-67.31				
		cc-pVTZ(72)	-0.05		-63.99				
		cc-pCVTZ(85)	-0.05		-62.79				

continued

Table 5. *Continued.*

Method	Compound	Basis	H	C	N	O	Si	S
		cc-pVQZ(145)	-0.05		-60.26			
		cc-pCVQZ(174)	-0.05		-60.26			
	H ₂ O	cc-pVDZ(24)	-0.72			-152.79		
		cc-pCVDZ(28)	-0.73			-173.70		
		cc-pVTZ(58)	-0.79			-163.72		
		cc-pCVTZ(71)	-0.79			-162.44		
		cc-VQZ(115)	-0.79			-159.98		
		cc-pCVQZ(144)	-0.79			-159.72		
		cc-pV5Z(201)	-0.80			-156.82		
	HNC	cc-pVDZ(33)	-0.16	60.64	-87.58			
		cc-pCVDZ(41)	-0.16	65.14	-101.32			
		cc-pVTZ(74)	-0.23	68.01	-101.71			
		cc-pCVTZ(100)	-0.23	64.85	-101.06			
		cc-pVQZ(140)	-0.26	65.24	-102.04			
		cc-pCVQZ(198)	-0.26	66.22	-103.11			
		cc-pV5Z(237)	-0.28	66.05	-102.82			
	NHC	cc-pVDZ(33)	-1.26	33.91	24.70			
		cc-pCVDZ(41)	-1.26	37.99	26.63			
		cc-pVTZ(74)	-1.62	39.80	28.59			
		cc-pCVTZ(100)	-1.62	38.04	27.94			
		cc-pVQZ(140)	-1.76	37.61	28.62			
		cc-pCVQZ(198)	-1.76	39.00	28.34			
		cc-pV5Z(237)	-1.82	32.38	28.48			
	HNCO	cc-pVDZ(47)	-0.17	-14.05	-44.81	-7.18		
		cc-pCVDZ(59)	-0.17	-15.34	-57.12	-7.64		
		cc-pVTZ(104)	-0.20	-16.00	-56.37	-10.43		
		cc-pCVTZ(143)	-0.21	-15.73	-57.34	-7.80		
		cc-pVQZ(195)	-0.19	-15.15	-56.21	-7.41		
	HCOOH ^a	cc-pVDZ(52)	0.03/ 0.18	-1.85		0.56/ -2.08		
		cc-pCVDZ(64)	0.02/ 0.18	-1.97		1.16/ -2.27		
		cc-pVTZ(118)	-0.01/ 0.014	-1.88		0.92/ -2.97		
	SiH ₃ ⁻	cc-pVDZ(33)	-0.12				-251.90	
		cc-pVTZ(76)	-0.08				-248.30	
	SiC ₂ ^b	cc-pVTZ(94)		-10.02/ 58.71			-14.54	
	H ₂ S	cc-pVDZ(28)	-1.03					-623.96
		cc-pVTZ(62)	-1.08					-610.91
		cc-pVQZ(119)	-1.13					-581.53
		cc-pV5Z(205)	-1.18					-628.09

^a See footnote to table 4.^b C/C in the linear structure corresponds to the C closer to Si/C farther from Si, respectively.

The Z^4 dependence, the basis set dependence, and the correlation contribution to the RHF values of the D1 term are similar to the description for the MV term, and therefore these trends are not discussed in detail here. The only exception is the faster convergence of E^{D1} relative to E^{MV} , with respect to the one-particle basis to the CBS limit [115].

4.3. The two-electron Darwin (D2) term

The two-electron Darwin (D2) correction term, as with the D1 term, serves to correct point-like charge distributions. Since it is a two-electron term, it reduces the repulsion between electrons. The energy correction E^{D2} , based on H^{D2} , is always negative. Because E^{D2} is proportional to the minuscule probability of two elec-

Table 6. RHF and CCSD(T) two-electron Darwin energy corrections ($E^{D2}/\mu E_h$) and CCSD(T) correlation energy contributions to E^{D2} ($\delta E^{D2}/\mu E_h$) for selected molecules at their equilibrium structures.^a

Compound	Basis	E^{D2}		δE^{D2}
		RHF	CCSD(T)	
C ₂ H ₆	cc-pVDZ(58)	-2 658	-2 635	-23
	cc-pCVDZ(66)	-2 656	-2 635	-21
	u-cc-pCVDZ(102)	-2 656	-2 427	-230
	cc-pVTZ(144)	-2 656	-2 560	-96
NH ₃	cc-pVDZ(29)	-2 197	-2 181	-16
	cc-pCVDZ(33)	-2 197	-2 064	-133
	u-cc-pCVDZ(51)	-2 198	-2 038	-160
	cc-pVTZ(72)	-2 198	-2 142	-56
	cc-pCVTZ(85)	-2 198	-2 009	-189
	u-cc-pCVTZ(103)	-2 198	-2 000	-198
	cc-pVQZ(145)	-2 198	-2 092	-106
	cc-pCVQZ(174)	-2 199	-1 970	-229
	cc-pVDZ(24)	-3 402	-3 381	-21
H ₂ O	cc-pCVDZ(28)	-3 403	-3 228	-175
	u-cc-pCVDZ(144)	-3 403	-3 191	-212
	cc-pVTZ(58)	-3 403	-3 340	-63
	cc-pCVTZ(71)	-3 405	-3 154	-251
	u-cc-CVTZ(87)	-3 405	-3 140	-265
	cc-pVQZ(115)	-3 405	-3 263	-142
	cc-pCVQZ(44)	-3 405	-3 098	-307
	cc-pV5Z(201)	-3 405	-3 243	-162
	HCN	cc-pVDZ(33)	-3 524	-3 506
cc-pCVDZ(41)		-3 523	-3 301	-222
u-cc-pCVDZ(67)		-3 524	-3 257	-267
cc-pVTZ(74)		-3 524	-3 439	-85
cc-pCVTZ(100)		-3 525	-3 208	-317
u-cc-pCVTZ(126)		-3 526	-3 192	-334
cc-pVQZ(140)		-3 526	-3 357	-169
cc-pCVQZ(198)		-3 526	-3 145	-381
cc-pV5Z(237)		-3 526	-3 331	-195
HNCO	cc-pVDZ(47)	-6 915	-6 877	-38
	cc-pCVDZ(59)	-6 914	-6 520	-394
	u-cc-pCVDZ(97)	-6 916	-6 438	-478
	cc-pVTZ(104)	-6 915	-6 767	-148
	cc-pCVTZ(143)	-6 918	-6 353	-565
	cc-pVQZ(195)	-6 919	-6 612	-307
HCOOH	cc-pVDZ(52)	-8 124	-8 079	-45
	cc-pCVDZ(64)	-8 123	-7 685	-438
	u-cc-pCVDZ(104)	-8 124	-7 592	-532
	cc-pVTZ(118)	-8 122	-7 963	-159
	cc-pCVTZ(157)	-8 127	-7 497	-630
SiH ₃ ⁻	cc-pVDZ(33)	-21 888	-21 877	-11
	CVDZ(72)	-21 885	-21 037	-848
	cc-pVTZ(76)	-21 890	-21 877	-50
	CVTZ(131)	-21 887	-20 977	-910
	cc-pVQZ(149)	-21 890	-21 851	-39
SiC ₂	cc-pVTZ(94)	-24 543	-24 431	-113
	CVDZ(111)	-24 542	-23 473	-1069
	cc-pVQZ(169)	-24 544	-24 375	-170
	CVTZ(193)	-24 544	-23 375	-1186

continued

Table 6. *Continued.*

Compound	Basis	E^{D2}		δE^{D2}
		RHF	CCSD(T)	
H ₂ S	cc-pVDZ(28)	-34 117	-34 102	-14
	cc-pVTZ(62)	-34 120	-34 074	-46
	CVDZ(65)	-34 115	-32 977	-1138
	CVTZ(115)	-34 117	-32 884	-1234
	cc-pVQZ(119)	-34 120	-34 059	-62
	CVQZ(193)	-34 118	-32 789	-1329
	cc-pV5Z(205)	-34 119	-33 930	-189

^a See footnote *a* to table 2.

trons being at the same point in space, it is expected to be small, and all E^{D2} energies collected in table 6 are consequently given in μE_h . While the E^{D2} values are certainly small, it is still important to establish the magnitude of the contribution of this term to the total (kinetic) relativistic energy correction, since (a) it appears to be the most important term neglected during the simple MVD1 treatment of relativistic effects, employed extensively for high precision model chemistry calculations, (b) it is closely related [29] to the spin-spin interaction term (see § 5.1), which is rarely considered [37–39], and (c) following the recipe of [41] and [42], it allows an estimation of the two-electron Lamb-shift correction.

As can be seen from table 6, the total D2 correction energy is given, to a very good degree of approximation, as a sum of atomic contributions, with $\{C, N, O, F, Ne\} = \{1300, 2200, 3400, 5000, 7100\} \mu E_h$ (the F and Ne data are taken from [115]). These numbers reveal a quasi- Z^3 dependence of the atomic contributions, in agreement with a Z^3 dependence that has been established for He-like systems [4]. (Using an accurate 50-term ($N_{\max} = 6$) Hylleraas expansion, one can obtain the following two-electron Darwin energies ($E^{D2}/\mu E_h$) for He-like systems: $\{He, Be^{2+}, C^{4+}, N^{5+}, O^{6+}, F^{7+}, Ne^{8+}, Ca^{18+}, Zn^{28+}, Sn^{48+}, Hg^{78+}\} = \{-17.82, -254.96, -1027.86, -1715.04, -2655.97, -3890.57, -5458.80, -48\ 276.59, -168\ 388.9, -800\ 252.2, -3326\ 223.6\}$, which reveal an asymptotic Z^3 dependence.) Although E^{D2} is only about 1% of the molecular E^{D1} contribution, and thus its neglect is usually reasonable, it is important to note that in the case of light molecules it has about the same order of magnitude as the correlation contribution to the D1 and MV values. It is also important to point out (table 7) that the contribution of E^{D2} to energy differences (barriers) is never larger than a few wavenumbers, and almost all of it is recovered at the RHF level.

The basis set convergence of E^{D2} has been studied in [115]. In particular, it was found that (a) convergence of E^{D2} employing HF wavefunctions is quick and (b) convergence of the correlation contribution seems to follow the form $\delta E^{D2}(X) = \delta E^{D2}(CBS) + cX^{-1}$, where X is the cardinal number of the correlation-consistent basis set, and CBS stands for the complete basis set limit. In all of our molecular examples we observe very quick convergence to the CBS RHF limit, and even the cc-pVDZ results differ from the CBS RHF limit by no more than a few μE_h . In clear contrast, but again in agreement with results of [115], the electron correlation contribution shows slow convergence. However, while Halkier *et al.* [115] investigated only the cc-pVXZ family of basis sets, in this study results are also available using the core-valence-corrected cc-pCVXZ family of basis sets. It is important to point out how different are the results obtained with the two basis set families. The most complete *ab initio* results are available for H₂O and HCN; therefore, we shall focus on only these two molecules. Use of a two-point extrapolation formula with two consecutive X values and an X^{-1} dependence results in the following limiting (VXZ, CVXZ) values for $\delta E^{D2}/\mu E_h$ at the CCSD(T) level: H₂O: $\{DT, TQ, Q5\} = \{(147, 403), (379, 475), (242,)\}$, and HCN: $\{DT, TQ, Q5\} = \{(219, 907), (421, 573), (299,)\}$. Thus the smooth and unambiguous X^{-1} convergence observed in [115] for the He atom and HF molecules (CCSD results) is not observed for the broader sample of molecules studied here.

4.4. The spin-own-orbit (SO) correction

As demonstrated in § 3.2, a part of the non-scalar effects of special relativity, the spin-own-orbit interaction, is accounted for by the Dirac-Coulomb or Coulomb-Pauli Hamiltonians. In closed-shell molecules the separated core and valence orbitals are fully occupied, and this interaction has no first-order effect on the

Table 7. RHF and CCSD(T) two-electron Darwin energy corrections ($\Delta E^{\text{D2}}/\mu E_{\text{h}}$) and CCSD(T) correlation energy contributions to ΔE^{D2} [$\delta(\Delta E^{\text{D2}})/\text{cm}^{-1}$] for barriers of selected compounds.

Compound	Basis	ΔE^{D2}		$\delta(\Delta E^{\text{D2}})$	
		RHF	CCSD(T)		
C ₂ H ₆ (eclipsed–staggered)	cc-pVDZ(58)	0.04	0.06	0.01	
	cc-pCVDZ(66)	0.06	0.06	0.00	
	u-cc-pCVDZ(102)	0.07	0.06	−0.01	
	cc-pVTZ(144)	0.08	−0.15	−0.23	
NH ₃ (planar–bent)	cc-pVDZ(29)	1.00	1.14	0.14	
	cc-pCVDZ(33)	1.24	1.27	0.03	
	u-cc-pCVDZ(51)	1.23	1.23	0.00	
	cc-pVT(72)	1.12	1.69	0.57	
	cc-pCVTZ(85)	1.11	1.11	0.00	
	u-cc-pCVTZ(103)	1.10	1.10	0.00	
	cc-pVQZ(145)	1.07	1.13	0.06	
	cc-pCVQZ(174)	1.06	1.04	−0.02	
H ₂ O (linear–bent)	cc-pVDZ(24)	2.32	2.69	0.37	
	cc-pCVDZ(28)	2.75	2.91	0.16	
	u-cc-pCVDZ(44)	2.82	2.92	0.04	
	cc-pVTZ(58)	2.57	3.01	0.44	
	cc-pCVTZ(71)	2.59	2.64	0.05	
	u-cc-pCVTZ(87)	2.60	2.62	0.02	
	cc-pVQZ(115)	2.53	2.65	0.12	
	cc-pCVQZ(144)	2.53	2.53	0.00	
	cc-pV5Z(201)	2.50	2.51	0.01	
	[H,C,N] (HNC–HCN)	cc-pVDZ(33)	0.12	0.11	−0.01
cc-pCVDZ(41)		0.32	0.29	−0.03	
u-cc-pCVDZ(67)		0.42	0.36	−0.06	
cc-pVTZ(74)		0.37	0.05	−0.32	
cc-pCVTZ(100)		0.43	0.35	−0.08	
u-cc-pCVTZ(126)		0.44	0.37	−0.07	
cc-pVQZ(140)		0.43	0.43	0.00	
cc-pCVQZ(198)		0.43	0.34	−0.09	
cc-pV5Z(237)		0.43	0.38	−0.05	
[H,C,N] (NHC (barrier)–HCN)		cc-pVDZ(33)	−1.68	−1.32	0.36
		cc-pCVDZ(42)	−1.78	−1.33	0.45
		u-cc-pCVDZ(67)	−1.69	−1.22	0.47
	cc-pVTZ(74)	−1.67	−2.64	−0.97	
	cc-pCVTZ(100)	−1.60	−1.21	0.39	
	u-cc-pCVTZ(126)	−1.60	−1.19	0.41	
	cc-pVQZ(140)	−1.59	−1.48	0.11	
	cc-pCVQZ(198)	−1.59	−1.21	0.38	
HNCO (linear–bent)	cc-pV5Z(237)	−1.60	−1.39	0.21	
	cc-pVDZ(47)	1.47	1.38	−0.09	
	cc-pCVDZ(59)	1.78	1.57	−0.21	
	u-cc-pCVDZ(97)	1.74	1.51	−0.23	
	cc-pVTZ(104)	1.72	2.56	0.84	
	cc-pCVTZ(143)	1.68	1.47	−0.21	
HCOOH (Z–E)	cc-pVQZ(195)	1.66	1.77	0.11	
	cc-pVDZ(52)	0.07	0.09	0.02	
	cc-pCVDZ(64)	0.04	0.10	0.06	
	u-cc-pCVDZ(104)	0.07	0.09	0.02	
	cc-pVTZ(118)	0.05	0.18	0.13	
	cc-pCVTZ(157)	0.06	0.07	0.01	

continued

Table 7. *Continued.*

Compound	Basis	ΔE^{D2}		$\delta(\Delta E^{\text{D2}})$
		RHF	CCSD(T)	
SiH ₃ ⁻ (planar–bent)	cc-pVDZ(33)	2.2	2.3	0.1
	CVDZ(72)	2.1	2.1	0.0
	cc-pVTZ(76)	2.7	2.7	0.0
	CVTZ(131)	2.5	2.5	0.0
	cc-pVQZ(149)	1.8	2.1	0.3
SiC ₂ (linear–T-shaped)	cc-pVTZ(94)	–0.5	–1.6	–1.2
	CVDZ(111)	–0.2	–1.2	–0.9
	cc-pVQZ(169)	–0.6	–1.2	–0.7
	CVTZ(193)	–0.3	–1.2	–0.9
H ₂ S (linear–bent)	cc-pVDZ(28)	4.5	5.2	0.7
	cc-pVTZ(62)	4.5	4.9	0.4
	CVDZ(65)	5.4	5.8	0.5
	CVTZ(115)	5.1	5.4	0.3
	cc-pVQZ(119)	4.3	4.7	0.4
	CVQZ(193)	5.1	5.3	0.2
	cc-pV5Z(205)	4.7	5.9	1.2

ground state energy. (This first-order effect becomes visible only when an electron is excited or ionized from this orbital. It also ‘switches on’ when the spin–orbit splitting becomes comparable with the corresponding bonding–antibonding orbital splitting.) Nevertheless, the spin–own-orbit term has a higher-order scalar effect on the ground state total energy, arising from spin–orbit interaction between occupied and empty shells [116]. In this study this scalar contribution has been obtained as the difference between the full four-component Dirac–Coulomb Hamiltonian and the four-component spin-free Dirac–Coulomb Hamiltonian of Dyal [112]. The contributions from this source are rather small, $+2.85 \mu E_{\text{h}}$ in the case of water, and $+423.72 \mu E_{\text{h}}$ in the case of H₂S, while its contributions to the barrier height are only -0.0094 cm^{-1} and -0.0086 cm^{-1} , respectively; consequently, it can safely be neglected. Nevertheless, because it scales approximately as $Z^{13/2}$ [112] it can cause considerable error if a spin-free theory is applied for molecules containing heavier elements. For example, for $Z = 40$ its value is about $168 \text{ m}E_{\text{h}}$ [112].

4.5. The ΔDPT correction term

The direct perturbation theory (DPT) of relativistic effects has been formulated by Sewell [75], Gesztesy *et al.* [76], Rutkowski [77], and Kutzelnigg [69–74]. According to the formulation of Kutzelnigg, the lowest order DPT correction (DPT(2)); since the perturbation expansion is given in power series of c^{-2} , the n th

order correction to the energy is usually noted as E_{2n} can be given as

$$E_2^{\text{DPT}} = c^{-2} \langle \chi_0 | (V - E_0) | \chi_0 \rangle, \quad (7)$$

$$\chi_0 = \frac{1}{2} \boldsymbol{\sigma} \cdot \mathbf{p} \Phi_0, \quad (8)$$

where E_0 and Φ_0 stand for the non-relativistic energy and wavefunction, respectively. It has been demonstrated by numerical calculations [71] that the main advantage of DPT(2) over MVD2 is its faster convergence to the one-particle basis set limit, as well as the non-divergent nature of the DPT($2n$) series. Furthermore, it has been shown by Kutzelnigg [74] that the DPT(2) term can be decomposed into the well known Pauli Hamiltonian plus a correction term,

$$\Delta E_2^{\text{DPT}} = \frac{1}{4} \langle \Phi_0 | [T, H_0 - E_0]_+ | \Phi_0 \rangle. \quad (9)$$

This ΔDPT term is responsible for the faster convergence of DPT(2) theory, and it vanishes at the basis set limit.

For the closed shell system studied here the spin–own-orbit interaction can be neglected, so that the ΔDPT terms were obtained simply as the difference of the total MVD2 and DPT(2) results. The DPT(2) and ΔDPT values are summarized in tables 8 and 9.

As expected from the above equation, the ΔDPT contribution is very small, and converges to zero with the basis set limit. Using the smallest correlation consistent basis set, cc-pVDZ, the numerical value of this term in the case of molecules containing first- and second-row

Table 8. $E^{\Delta\text{DPT}}$ corrections (in mE_h) to total energies of selected molecules at their equilibrium structures.

Compound	Basis	$E^{\Delta\text{DPT}}$	
		RHF	CCSD(T)
C_2H_6	cc-pVDZ(58)	0.037	0.029
	cc-pCVDZ(66)	0.000	0.005
	u-cc-pCVDZ(102)	0.000	-0.002
	cc-pVTZ(144)	-0.019	-0.057
NH_3	cc-pVDZ(29)	0.018	0.009
	cc-pCVDZ(33)	-0.015	-0.013
	u-cc-pCVDZ(51)	0.002	0.000
	cc-pVTZ(72)	-0.003	-0.034
	cc-pCVTZ(85)	0.003	0.035
	u-cc-pCVTZ(103)	0.001	-0.001
	cc-pVQZ(145)	-0.012	-0.008
	cc-pCVQZ(174)	-0.012	-0.006
H_2O	cc-pVDZ(24)	0.007	-0.007
	cc-pCVDZ(28)	0.005	0.006
	u-cc-pCVDZ(44)	0.001	0.001
	cc-pVTZ(58)	0.988	-0.041
	cc-pCVTZ(71)	-0.611	0.045
	u-cc-pCVTZ(87)	-0.001	-0.002
	cc-pVQZ(115)	-0.002	0.004
	cc-pCVQZ(144)	0.024	0.033
	cc-pV5Z(201)	-0.036	-0.009
	cc-pVDZ(33)	0.048	0.049
HCN	cc-pCVDZ(41)	0.033	0.032
	u-cc-pCVDZ(67)	0.002	0.000
	cc-pVTZ(74)	-0.003	-0.056
	cc-pCVTZ(100)	-0.002	0.049
	u-cc-pCVTZ(126)	-0.001	-0.002
	cc-pVQZ(140)	-0.004	-0.004
	cc-pCVQZ(198)	-0.004	0.006
	cc-pV5Z(237)	0.012	0.048
	cc-pVDZ(47)	0.061	0.035
	cc-pCVDZ(59)	0.041	0.038
HNCO	u-cc-pCVDZ(97)	0.004	-0.001
	cc-pVTZ(104)	-0.029	-0.118
	cc-pCVTZ(143)	-0.004	0.089
	cc-pVQZ(195)	-0.006	0.003
	cc-pVDZ(52)	0.051	0.013
HCOOH	cc-pCVDZ(64)	0.031	0.027
	u-cc-pCVDZ(104)	0.003	0.000
	cc-pVTZ(118)	-0.068	-0.159
	cc-pVDZ(33)	-0.056	-0.058
SiH_3^-	CVDZ(72)	0.007	0.015
	cc-pVTZ(76)	-0.015	-0.063
	CVTZ(131)	0.026	0.025
	cc-pVQZ(149)	0.053	0.014
SiC_2	cc-pVTZ(94)	0.002	-0.094
	CVDZ(111)	0.004	-0.009
	cc-pVQZ(169)	0.017	-0.006
	CVTZ(193)	-0.002	-0.004
H_2S	cc-pVDZ(28)	-0.020	-0.011
	cc-pVTZ(62)	0.017	-0.024
	CVDZ(65)	-0.020	0.029
	CVTZ(115)	0.097	0.094
	cc-pVQZ(119)	-0.022	-0.349
	CVQZ(193)	0.007	-0.001
cc-pV5Z(205)	-0.046	-0.036	

Table 9. $\Delta E^{\Delta\text{DPT}}$ corrections (in cm^{-1}) to barriers of selected molecules.

Compound	Basis	$\Delta E^{\Delta\text{DPT}}$		
		RHF	CCSD(T)	
C_2H_6 (eclipsed-staggered)	cc-pVDZ(58)	0.04	0.01	
	cc-pCVDZ(66)	-0.01	-0.04	
	u-cc-pCVDZ(102)	0.01	-0.01	
	cc-pVTZ(144)	-0.26	-0.45	
NH_3 (planar-bent)	cc-pVDZ(29)	3.58	2.74	
	cc-pCVDZ(33)	0.31	0.15	
	u-cc-pCVDZ(51)	-0.01	0.00	
	cc-pVTZ(72)	-0.86	-1.10	
	cc-pCVTZ(85)	-0.12	-1.29	
	u-cc-pCVTZ(103)	-0.01	-0.02	
	cc-pVQZ(145)	-0.33	-0.58	
	cc-pCVQZ(174)	0.06	0.04	
H_2O (linear-bent)	cc-pVDZ(24)	7.45	5.27	
	cc-pCVDZ(28)	0.40	-0.02	
	u-cc-pCVDZ(44)	-0.01	0.01	
	cc-pVTZ(58)	0.74	-0.45	
	cc-pCVTZ(71)	1.12	0.82	
	u-cc-pCVTZ(87)	-0.03	-0.01	
	cc-pVQZ(115)	-0.76	-0.47	
	cc-pCVQZ(144)	0.00	-0.04	
	cc-pV5Z(201)	0.30	-0.37	
	[H, C, N]	cc-pVDZ(33)	1.92	1.26
HNC-HCN	cc-pCVDZ(41)	-1.20	-1.08	
	u-cc-pCVDZ(67)	-0.08	-0.07	
	cc-pVTZ(74)	1.50	1.25	
	cc-pCVTZ(100)	0.61	0.49	
	u-cc-pCVTZ(126)	-0.01	0.02	
	cc-pVQZ(140)	-0.54	-0.06	
	cc-pCVQZ(198)	0.06	0.08	
	cc-pV5Z(237)	-0.02	0.01	
	[H, C, N]	cc-pVDZ(33)	-2.17	-3.28
	NHC (barrier)-HCN	cc-pCVDZ(41)	-1.70	-1.73
u-cc-pCVDZ(67)		-0.05	-0.06	
cc-pVTZ(74)		1.41	1.60	
cc-pCVTZ(100)		-0.05	0.21	
u-cc-pCVTZ(126)		0.06	0.06	
cc-pVQZ(140)		0.06	-0.47	
cc-pCVQZ(198)		0.06	0.11	
cc-pV5Z(237)		0.04	-0.04	
HNCO (linear-bent)		cc-pVDZ(47)	5.38	4.59
cc-pCVDZ(59)		1.22	1.11	
u-cc-pCVDZ(97)	0.03	0.01		
cc-pVTZ(104)	-1.58	-1.97		
cc-pCVTZ(143)	-0.14	-0.32		
cc-pVQZ(195)	0.24	1.00		
HCOOH (Z-E)	cc-pVDZ(52)	-0.26	-0.02	
	cc-pCVDZ(64)	-0.06	-0.02	
	u-cc-pCVDZ(104)	0.02	0.04	
	cc-pVTZ(118)	-0.11	0.01	
SiH_3^- (planar-bent)	cc-pVDZ(33)	4.8	5.8	
	CVDZ(72)	0.1	0.1	
	cc-pVTZ(76)	6.7	6.0	
	CVTZ(131)	0.0	0.1	
	cc-pVQZ(149)	11.0	8.4	

continued

Table 9. *Continued.*

Compound	Basis	$\Delta E^{\Delta\text{DPT}}$	
		RHF	CCSD(T)
SiC ₂ (linear–T-shaped)	cc-pVTZ(94)	4.2	4.8
	CVDZ(111)	–0.1	0.1
	cc-pVQZ(169)	2.5	2.3
H ₂ S (linear–bent)	CVTZ(193)	0.1	0.0
	cc-pVDZ(28)	1.0	3.3
	cc-pVTZ(62)	11.5	9.6
	CVDZ(65)	–0.1	0.0
	CVTZ(115)	–0.1	–0.1
	cc-pVQZ(119)	22.7	18.9
	CVQZ(193)	–0.2	0.0
	cc-pV5Z(205)	7.8	3.3

elements can reach only some $10\mu E_h$ and $1mE_h$, respectively. Using the cc-pVDZ basis the ΔDPT contribution to the barriers for molecules containing first- and second-row atoms can be as high as $5\text{--}10\text{ cm}^{-1}$ and over 10 cm^{-1} , respectively, while usually it is negligible, and is below the numerical accuracy of our calculations for $X \geq 4$. Unexpectedly, the ΔDPT term usually increases the error of the MVD2 relativistic energy correction calculated with the smallest basis sets, but in most cases it significantly reduces the error of the energy differences. For example, it reduces the deviation of the MVD2 result obtained with the cc-pVDZ basis set from the basis set limit from $50\text{--}30\%$ to $30\text{--}10\%$. Furthermore, the absolute value of this term seems to be a good indicator of the quality of the basis set used for the relativistic calculations. Nevertheless, in certain cases, especially in the case of molecules containing only first-row elements, this term was found to be smaller for

the smallest basis sets than for better quality ones (e.g. cc-pVDZ versus cc-pCVTZ for water). Therefore, it appears that $E^{\Delta\text{DPT}} = 0$ is a necessary but not sufficient condition to declare a basis set well suited to *ab initio* calculations of relativistic effects.

4.6. Accuracy of perturbative treatments: comparison with four-component variational Dirac–Hartree–Fock results

The various relativistic energy corrections obtained by perturbation theory and the corresponding variational results, obtained with the smallest uncontracted basis sets and the RHF method, are presented in tables 10 and 11. As can be seen from these data, for molecules containing only first-row elements the error of the MVD1, MVD2, and DPT(2) theories for total energies are, respectively, $7\text{--}13\%$, 0.1% , and 0.1% . For molecules containing second-row elements the corresponding values are, respectively, $3\text{--}5\%$, 0.5% , and 0.5% . The values obtained for DPT(2) theory are in very good agreement with the values presented for closed-shell atoms by Ottshofski and Kutzelnigg [73]. The corresponding errors in the case of the barrier heights are (first-row systems) $2\text{--}5\%$, $0.1\text{--}0.2\%$, and $0.1\text{--}0.2\%$ and (second-row systems) $3\text{--}4\%$, $1\text{--}2\%$, and $1\text{--}2\%$, which correspond to absolute errors of less than (first-row systems) 3 , 0.25 , and 0.25 cm^{-1} and (second-row systems) 10 , 4 , and 4 cm^{-1} (the quoted errors correspond, respectively to the MVD1, MVD2, and DPT(2) theories). Additionally, we have investigated the performance of the MVD2 and DPT(2) methods over the semi-global PES of water. Using the larger basis set described in [117] and making computations at the 325 grid points of [36], the largest relative error (i.e. maxi-

Table 10. Kinetic relativistic energy corrections (in mE_h) to total energies of selected molecules at their equilibrium structures as obtained by different methods at the HF level of theory.^a

Compound	Basis	E^{MVD1}	E^{MVD2}	$E^{\text{DPT(2)}}$	E^{DHF}
C ₂ H ₆	u-cc-pCVDZ	–29.175	–31.831	–31.831	–31.853
NH ₃	u-cc-pCVDZ	–28.697	–30.895	–30.893	–30.926
	u-cc-pCVTZ	–28.752	–30.950	–30.951	–30.983
H ₂ O	u-cc-pCVDZ	–51.499	–54.902	–54.901	–54.980
	u-cc-pCVTZ	–51.622	–55.027	–55.028	–55.108
HCN	u-cc-pCVDZ	–43.634	–47.158	–47.156	–47.200
	u-cc-pCVTZ	–43.705	–47.231	–47.232	–47.276
HNCO	u-cc-pCVDZ	–95.039	–101.955	–101.951	–102.074
HCOOH	u-cc-pCVDZ	–117.755	–125.879	–125.876	–126.046
SiH ₃ [–]	CVDZ	–599.72	–621.60	–621.59	–624.59
SiC ₂	CVDZ	–629.42	–654.46	–654.46	–657.48
H ₂ S	CVDZ	–1075.44	–1109.55	–1109.53	–1116.56

^a E^{DHF} results have been obtained as the difference between calculations using the speed of light $c = 137.0359895\text{ au}$ and $c = 10\,000.0\text{ au}$.

Table 11. Kinetic relativistic energy corrections (in cm^{-1}) to barriers of selected molecules at their equilibrium structures as obtained by different methods at the HF level of theory.^a

Compound	Basis	ΔE^{MVD1}	ΔE^{MVD2}	$\Delta E^{\text{DPT(2)}}$	ΔE^{DHF}
C ₂ H ₆	u-cc-pCVDZ	0.52	0.58	0.57	0.57
NH ₃	u-cc-pCVDZ	22.98	24.21	24.20	24.26
	u-cc-pCVTZ	20.87	21.97	21.96	22.02
H ₂ O	u-cc-pCVDZ	59.50	62.32	62.31	62.50
	u-cc-pCVTZ	54.18	56.78	56.75	56.92
HNC	u-cc-pCVDZ	15.36	15.78	15.70	15.69
	u-cc-pCVTZ	14.83	15.27	15.26	
NHC	u-cc-pCVDZ	-31.41	-33.10	-33.15	-33.31
	u-cc-pCVTZ	-30.89	-32.49	-32.43	
HNCO	u-cc-pCVDZ	31.95	33.69	33.72	33.85
HCOOH	u-cc-pCVDZ	0.35	0.42	0.44	0.44
SiH ₃ ⁻	CVDZ	102.9	105.6	105.7	104.5
SiC ₂	CVDZ	-1.0	-1.2	-1.3	-3.5
H ₂ S	CVDZ	227.3	232.6	232.6	234.8

^a See footnote to table 10.

imum difference – minimum difference) of the MVD2 approach is 0.76 cm^{-1} , while it is only 0.66 cm^{-1} in the case of the DPT(2) method, as compared with the four-component fully variational results. (Note that the full extent of the relativistic energy correction at this grid exceeds 100 cm^{-1} .)

5. Corrections beyond Dirac–Coulomb theory

5.1. Relativistic correction of the Coulomb potential: the spin–spin, the Gaunt and the Breit interactions

The difference between the Dirac–Breit and the Dirac–Coulomb operators contains terms of the order of $Z^2\alpha^2$, which has several consequences. First, as it scales similarly to the $O(\alpha^2)$ kinetic relativistic correction, the neglect of this term can introduce undesired inaccuracies; second, as it scales only with Z^2 , its relative importance is more pronounced for light molecular systems.

There are few computational studies of Gaunt or Breit correction effects on light molecular systems. These include the correction to the equilibrium electronic energy [118] and to the potential energy hypersurface and rovibrational energy levels of water [117], and the correction to the equilibrium energies, geometries and harmonic frequencies of dihalogenides [114, 119] and hydrogen halogenides [120, 121]. These studies indicate that, for high- Z systems, the energy correction due to the correction of the Coulomb potential is negligible compared with the kinetic relativistic corrections. Nevertheless, it becomes important if high accuracy is required, even for low- Z systems.

The Breit correction within the Pauli approximation has been considered in only a few studies, e.g. by Davidson [29, 33]. These studies exploit the theoretical

feature that the leading term not considered in the Pauli–Coulomb Hamiltonian for closed shell systems is the H^{SS} term (equation (5f) of this study). Furthermore, this term can be approximated by neglecting the H^{DP} dipolar interaction term which, upon substitution of $\langle(\sigma_1 \cdot \sigma_2)\rangle = -3/4$ into equation (5f) leads to the equation $H^{\text{SS}} \approx H^{\text{FC}} = -2 \times H^{\text{D2}}$ [122]. The simple analytical treatment of He-like systems demonstrates the validity of this approximation for spherical systems. For {He, Be²⁺, C⁴⁺, N⁵⁺, O⁶⁺, F⁷⁺, Ne⁸⁺, Na⁹⁺, Mg¹⁰⁺} the Breit energies (at the DHF level, in μE_h) are {63.777, 257.75, 666.20, 1369.1, 2446.7, 3979.1, 6046.7, 8730.1, 12110}, while the values of the corresponding approximate spin–spin term are {63.974, 258.41, 667.52, 1371.2, 2449.3, 3981.6, 6048.2, 8728.8, 12103} for this isoelectronic series.

The approximate spin–spin term, together with the Gaunt and Breit energy corrections obtained at the RHF level for the molecules studied in this work, are collected in tables 12 and 13. The Gaunt contribution to the total kinetic relativistic correction is between 14–17% for molecules containing first-row elements only, and 7–10% for molecules containing second-row elements as well. The retardation effect ($E^{\text{Breit}} - E^{\text{Gaunt}}$) lowers these contributions only by about 1% in both cases. The situation is quite different for calculated corrections to barrier heights. In this case the retardation correction can be as large as the Gaunt correction. In the case of the E - Z isomers of HCOOH the signs of the Gaunt and Breit corrections are opposite. However, it should be noted that in [117] and [118] it was shown for water that the Gaunt energy correction varies mainly with the bond lengths and the retardation energy correction depends somewhat more on the bond angles. There-

Table 12. Approximate spin–spin (SS), Gaunt, and Breit energy corrections (in mE_h) to total energies of selected molecules at their (lowest energy) equilibrium structures as determined at the HF level.

Compound	Basis	E^{SS}	E^{Gaunt}	E^{Breit}
C ₂ H ₆	u-cc-pCVDZ	5.312	5.818	5.672
NH ₃	u-cc-pCVDZ	4.396	4.491	4.785
	u-cc-pCVTZ	4.396	4.951	4.792
H ₂ O	u-cc-pCVDZ	6.806	7.868	7.568
	u-cc-pCVTZ	6.810	7.886	7.582
HCN	u-cc-pCVDZ	7.048	7.794	7.573
	u-cc-pCVTZ	7.052	7.808	7.584
HNCO	u-cc-pCVDZ	13.832	15.658	15.134
HCOOH	u-cc-pCVDZ	16.248	18.591	17.924
SiH ₃ [−]	CVDZ	43.770	58.826	54.859
SiC ₂	CVDZ	49.084	64.519	60.427
H ₂ S	CVDZ	68.230	94.516	87.639

Table 13. Approximate spin–spin (SS), Gaunt, and Breit energy corrections (in cm^{-1}) to *barriers* of selected molecules at their (lowest energy) equilibrium structures as determined at the HF level.

Compound	Basis	ΔE^{SS}	ΔE^{Gaunt}	ΔE^{Breit}
C ₂ H ₆	u-cc-pCVDZ	−0.13	−0.19	−0.22
NH ₃	u-cc-pCVDZ	−2.46	2.32	1.47
	u-cc-pCVTZ	−2.20	2.33	1.50
H ₂ O	u-cc-pCVDZ	−5.64	5.81	3.77
	u-cc-pCVTZ	−5.20	5.76	3.77
HNC	u-cc-pCVDZ	−0.84	2.36	1.80
	u-cc-pCVTZ	−0.88	2.34	1.77
NHC	u-cc-pCVDZ	3.38	−1.44	−0.77
	u-cc-pCVTZ	3.20	−1.69	−0.98
HNCO	u-cc-pCVDZ	−3.48	2.78	1.69
HCOOH	u-cc-pCVDZ	−0.14	0.25	−0.23
SiH ₃ [−]	CVDZ	−4.2	4.58	2.84
SiC ₂	CVDZ	0.5	−0.59	−0.40
H ₂ S	CVDZ	−10.7	12.23	8.09

fore, the present numerical data for barrier heights represent a case where the retardation correction is relatively large.

A spherically symmetric operator, like H^{FC} , is not sensitive to changes in the geometry, and particularly not to changes in bond angles. Consequently, the neglected spherically non-symmetric operators are responsible for describing the molecular contributions to atomic sums, and for the changes in the Breit energy over the PES. As a consequence, the approximation of the Breit interaction by the H^{FC} term is less satisfactory than the approximation of the Dirac–Coulomb Hamiltonian by the Coulomb–Pauli Hamiltonian. For total energies the approximate spin–spin

term results in only about 80–90% of the Breit energies. For calculated barrier heights the results are far worse, and in most cases even the signs of the corrections are wrong.

5.2. Lamb-shift contributions

As mentioned in § 1, the Dirac–Coulomb–Gaunt/Breit/Brown Hamiltonian is accurate to terms of order $Z^2\alpha^2$. To achieve a higher accuracy within an *ab initio* treatment radiative corrections to the energy levels must be calculated explicitly within the framework of relativistic QED. QED theory is too tedious for routine use in many-electron molecular systems and no practically realizable scheme has yet been developed to handle the

Table 14. Approximate one- and two-electron Lamb-shift energy corrections (ΔE^{L1} , ΔE^{L2} in cm^{-1}) to barriers.

Compound	Wavefunction of Darwin terms	ΔE^{L1}	ΔE^{L2}
C ₂ H ₆	cc-pVTZ CCSD(T)	-0.05	-0.01
NH ₃	cc-pCVQZ CCSD(T)	-1.41	0.06
H ₂ O	cc-pV5Z CCSD(T)	-3.54	0.13
HNC	cc-pV5Z CCSD(T)	-0.75	0.02
NHC	cc-pV5Z CCSD(T)	1.39	-0.07
HNCO	cc-pVQZ CCSD(T)	-1.87	0.09
HCOOH	cc-pVTZ CCSD(T)	-0.09	0.01
SiH ₃ ⁻	cc-pVTZ CCSD(T)	-3.75	0.11
SiC ₂	cc-pVTZ CCSD(T)	1.01	-0.08
H ₂ S	cc-pV5Z CCSD(T)	-8.52	0.31

required renormalizations of mass and charge for systems other than one-electron central-field ions. Therefore, it is worth exploring approximate treatments of the leading QED effects. The main contribution term of QED beyond the Dirac–Coulomb–Gaunt/Breit/Brown Hamiltonian is the one-electron Lamb shift, which scales as $Z^4\alpha^3$ for low- Z systems [123, 124]. According to the approach of [42], approximate values of the one- and two-electron Lamb-shift contributions can be obtained simply by rescaling the D1 and D2 energy corrections, respectively. In table 14 the one- and two-electron Lamb-shift corrections are reported for those molecules where they are available at the cc-pCVQZ CCSD(T) level. More values can be obtained readily by using [42], table II and our tables 4 and 5. As can be seen from table 14, the one-electron Lamb-shift correction can reach a few cm^{-1} for barrier heights, while the two-electron Lamb-shift corrections are negligible.

6. Conclusion

The most notable results of this extensive computational study are as follows.

A large number of relativistic energy computations have been performed, both at the simple Hartree–Fock level and, when applicable, at the highly correlated coupled-cluster [CCSD(T)] level, for the light molecular systems C₂H₆, NH₃, H₂O, [H,C,N], HNCO, HCOOH, SiH₃⁻, SiC₂, and H₂S. The absolute energy corrections obtained resulted from different relativistic treatments, including the Dirac–Coulomb and Dirac–Breit Hamiltonians, together with an approximate treatment of the Lamb-shift effect of quantum electrodynamics. Our calculations suggest, in line with previous studies, that the largest absolute energy correction results from the Dirac–Hartree–Fock treatment (the energy correction is very nearly a sum of atomic contributions, which is a simple consequence of the fact that almost all of the

relativistic energy correction is associated with the core orbitals), followed by the Breit and Lamb-shift correction energies.

In an effort to understand the geometry dependence of relativistic energy corrections, the contribution of all relativistic terms on inversion barriers (NH₃ and SiH₃⁻), rotational barriers (C₂H₆), barriers to linearity (H₂O, H₂S, and HNCO), conformational energy differences (HCOOH, SiC₂), and isomerization barrier ([H,C,N] system) have been established. In all cases studied except C₂H₆, especially where substantial rehybridization of the valence shell occurs between the two reference forms, the relativistic energy correction is substantial, and thus cannot be neglected in high accuracy theoretical treatments.

Although the procedure has its limitations [42], the atomic contributions to the total one-electron Darwin energy correction, E^{D1} , have been used to obtain approximate one-electron Lamb-shift energy corrections.

Although in absolute terms the two-electron Darwin energy correction E^{D2} is not substantial, its magnitude is about the same as the correlation contribution to the E^{MV} and E^{D1} energy corrections. Therefore, when the effect of electron correlation on relativistic energies is considered, E^{D2} should preferably be computed. It should be noted also that the energy correction due to the Breit interaction is also of this magnitude.

We observed no clear basis set convergence for either the relativistic HF energies or for the related correlation contributions in any of our calculations for the mass-velocity energy correction term E^{MV} . This and a similar lack of convergence in E^{D1} calculations suggest that the correlation-consistent basis sets of Dunning, which were proved to have extraordinary convergence characteristics in non-relativistic treatments, do not seem to be similarly well suited for converged relativistic energy calculations. Convergence characteristics of Gaussian basis sets for relativistic treatments should be investigated further.

The condition $E^{\Delta DPT} \cong 0$ is necessary but not sufficient to decide whether a basis set is suitable for obtaining converged relativistic energy corrections.

The performance of the simple {MVD1, MVD2, and DPT(2)} approximate treatments for light molecular systems has been found to range between ‘very good’ and ‘excellent’ when compared with the full four-component Dirac–Hartree–Fock (DHF) theory. For total energies the errors are, respectively, {7–13%, 0.1% and 0.1%} for molecules containing first-row elements only, while for molecules containing second-row elements they are {3–5%, 0.5%, and 0.5%}. The corresponding values in the case of the barrier heights are {2–5%, 0.1–0.2% and 0.1–0.2%} and {3–4%, 1–2% and 1–

2%}, respectively. These results confirm that first-order corrections are adequate for understanding relativistic corrections to energies of light molecular systems, and thus suggest that first-order treatments should hold a prominent place in relativistic calculations for first- and second-row systems.

Using the spin–spin term of the Pauli Hamiltonian instead of the Breit interaction is not a good approximation. For total energies the spin–spin term results in 80–90% of the Breit energies, and the situation is even worse for relative energies along the PES.

The Gaunt contribution to the total kinetic relativistic energy correction is between 14–17% for molecules containing first-row elements only, and 7–10% for molecules containing second-row elements as well.

In extreme cases the discrepancy between the Gaunt and Breit energy corrections can be as large as 50%.

The one-electron Lamb-shift energy correction can reach a few cm^{-1} for barriers, while the two-electron Lamb-shift energy corrections seems to be negligible.

The authors would like to thank Professors P. Pyykkö and W. D. Allen for helpful discussions. The work of G.T. and A.G.C. has been partially supported by the Hungarian Ministry of Culture and Education (FKFP 0117/1997) and by the Hungarian Scientific Research Fund (OTKA T024044 and T033074). The research by W.K. has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences. A grant of computer time by the Academic Computing Services Amsterdam (SARA) is gratefully acknowledged. H.M.Q. wishes to acknowledge the hospitality of the School of Chemistry (Melbourne) and the research facilities made available by Professors F. P. Larkins and K. P. Ghiggino.

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