

Perspective: Relativistic effects

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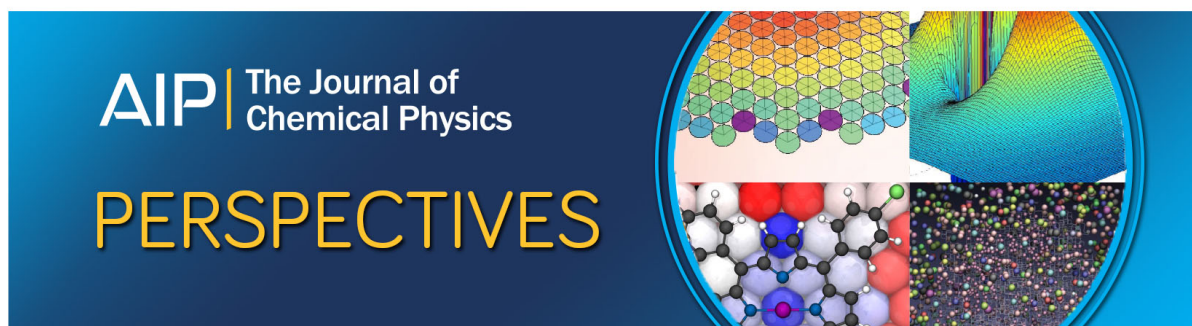
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Perspective: Relativistic effects

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This perspective article discusses some broadly-known and some less broadly-known consequences of Einstein's special relativity in quantum chemistry, and provides a brief outline of the theoretical methods currently in use, along with a discussion of recent developments and selected applications. The treatment of the electron correlation problem in relativistic quantum chemistry methods, and expanding the reach of the available relativistic methods to calculate all kinds of energy derivative properties, in particular spectroscopic and magnetic properties, requires on-going efforts. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3702628>]

I. WHAT ARE RELATIVISTIC EFFECTS?

Relativistic quantum chemistry is a research field that once bordered on the obscure. It has made enormous strides in the past decades. These days, many chemists are aware of relativistic effects in structural chemistry and spectroscopy. Some relativistic quantum chemistry software packages have become quite user friendly, enabling non-specialists to perform all-electron relativistic quantum chemical calculations routinely. Various undergraduate textbooks and educational articles now discuss relativistic effects (e.g., Refs. 1–4 and later editions of the cited textbooks). However, continuing efforts are required to raise the awareness in the chemistry community of (i) the impact of relativity on chemistry beyond discussing the celebrated consequences of relativity on the yellow color of solid gold and the low melting point of mercury, and (ii) new developments of relativistic quantum chemical methods which allow for increasingly accurate calculations and give access to an increasing number of molecular spectroscopic properties. As an example for point (i), an article in *Nature* (London) by Gagliardi and Roos reporting calculations for the U_2 diatomic has received much attention.⁵ According to the study, in U_2 there are three two-electron and four one-electron bonds, adding up to a quintuple bond for the septet ground state. Uranium is the heaviest naturally occurring element, and relativistic effects play a major role in U_2 and other actinide systems. Or consider the element lead: As Ahuja *et al.* have recently found, relativistic effects account for 1.7–1.8 V in a standard 2-V lead-acid battery cell.⁶ In the authors' words, “cars start due to relativity.”

Nature (not the journal) is relativistic, that is, Einstein relativistic as opposed to Galilei relativistic (nonrelativistic), due to the finite rather than an infinite speed of light. For the purpose of this article, *relativistic effects* are defined as the differences between results of (four-component or two-component or one-component “scalar”) relativistic quantum theoretical calculations using a finite and an infinite speed of light, respectively, with results from the latter being equivalent to results from conventional nonrelativistic calculations based on the Schrödinger equation. Thus, relativistic effects

are generally not observable in the sense of the usual observables of quantum theory such as position, momentum, energy, etc. However, manifestations of relativistic effects in the chemistry and physics of heavy elements compounds are ubiquitous. In the case when an atomic or molecular property vanishes in the nonrelativistic limit (such as spin-orbit coupling or electronic g -shifts (deviations from the free-electron g value)), then the consequences of relativity are directly observable.

At the size scale of atoms and molecules, and given the small masses of protons, neutrons, and electrons, gravitational effects on chemical phenomena can be neglected. **In relativistic quantum chemistry one deals with Einstein's special relativity. The effects become apparent as the velocities of the particles approach the speed of light c .** Consider a free electron. Nonrelativistically, the energy of a free particle is $W^{\text{nr}} = p^2/2m = mv^2/2$ where m is the rest mass of the electron, $p = mv$ is the linear momentum, and v is the velocity. According to Einstein, $W^{\text{rel}} = (p^2c^2 + m^2c^4)^{1/2} = mc^2 + p^2/2m - p^4/8m^3c^2 + \dots$ where p is now the relativistic momentum. The rest-mass energy mc^2 shifts the origin of the energy scale. Relativistic correction factors (relative corrections) to the kinetic energy are of leading order c^{-2} and increase with the momentum squared of the particle. For an electron in the field of a nucleus with charge Ze the nonrelativistic kinetic energy, being proportional to the momentum-squared expectation value, is proportional to Z^2 . The leading order relativistic correction factors of the electron energies therefore go as Z^2/c^2 where, in atomic units, $c \approx 137$, leading to an approximately Z^4 behavior of the relativistic energies of one-electron atoms. One may speculate, as some have done,⁷ that relativistic effects on the chemical properties of heavy atoms are small because their valence shells are subject to small effective (screened) nuclear charges. This turns out to be incorrect;⁸ valence orbitals in heavy many-electron atoms have comparatively small orbital energies but may have very large kinetic and potential energies. As a result, in many-electron atoms and molecules the leading order of relativistic effects for valence orbitals is also Z^2/c^2 with Z being the full charge of the heaviest nucleus. Relativistic effects on electronic structures increase with the full, not the screened, charges of the nuclei in the system.

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Depending on the desired accuracy of a calculation, relativistic effects may be required even for light elements^{9–12} (H, C, N, O, etc., with C, N, and O curiously sometimes termed “heavy atoms” in the computational chemistry literature). For truly heavy atoms such as I, Cs, Pt, Au, Hg, Pb, U, and so on, $(Z/c)^2$ reaches an appreciable magnitude, and relativistic effects may alter the chemical and physical behavior *qualitatively*. The chemistry of light elements is well described by nonrelativistic quantum mechanics, whereas heavy elements require a relativistic theory. In particular, in the lower third of the periodic table, the chemical characteristics of the elements are strongly influenced by relativity.^{13,14} For example, lighter group 13 and 14 elements such as Al, Ga, Si, Ge, tend to favor oxidation states of III and IV, respectively, whereas the heaviest members of the groups, Tl and Pb, favor the oxidation states I and II, respectively. The rationale for such changes in the chemical behavior when going down in the group is the particular energetic stabilization of the valence *s* orbital in Tl, Pb, and other heavy 6th row elements due to relativistic effects, creating the 6*s* “inert pair” effect.¹⁵ A large number of such chemical trends, and many other manifestations of relativistic effects in chemistry, have been cataloged and rationalized by Pyykkö.^{16–18}

Thus, relativistic effects can be observed in chemical trends, for instance, when compounds with light and heavy elements from the same group of the periodic table are compared. There are also well-known “heavy atom effects” in spectroscopy. For instance, in NMR spectroscopy the presence of a heavy halide (Br, I) bound to a light atom causes the chemical shift of the light atom to be more negative (more shielded) than in an analogous compound with Cl or F. This so-called normal halogen dependence has been known for quite some time¹⁹ to be caused by spin-orbit (SO) coupling,²⁰ which is a relativistic effect. SO coupling also leads to the splitting of multiplet levels that would be degenerate according to nonrelativistic theory, and it is therefore directly observed in atomic spectroscopy. Relativistic effects need not be minor corrections on top of the nonrelativistic result, as the expansion of the energy in orders of c^{-2} above may suggest. For instance, relativistic effects on nucleus-electron hyperfine coupling constants or on NMR *J*-coupling constants involving heavy elements such as ¹⁹⁹Hg may well exceed the magnitude of the corresponding nonrelativistic value²¹ (sometimes by a factor of three or more). Mössbauer isomer shifts have also been associated with extremely large relativistic effects.¹⁸ The difference between relativistic and nonrelativistic theory can therefore mean the difference between “(approximately) correct” and “qualitatively wrong.” Even though bond lengths, bond angles, valence orbital energies, and other chemically relevant quantities may change less drastically than NMR or EPR parameters due to relativity, percentage-wise, the difference can mean a correct versus an incorrect prediction of the chemical behavior and spectroscopic properties of a heavy element compound.

In Secs. II and III, an account of some commonly applied relativistic quantum chemistry methods is provided (Sec. II), along with some representative examples from structural chemistry and spectroscopy (Sec. III). For the scope of this perspective on relativistic effects, neither of

these sections is intended to provide an exhaustive coverage of the literature but rather to illustrate the overall approach and some of the more iconic relativistic effects known in chemistry. References to review articles are provided where the reader can find additional information and a more complete coverage of the literature. The material presented herein reflects the author’s personal experience. A brief outlook is provided in Sec. IV. Unless stated otherwise, we use dimensionless atomic units,²² such that $m_e = 1$, $\hbar = 1$, $e = 1$, $4\pi\epsilon_0 = 1$, and $c = 137.0359976(50) = \alpha^{-1}$ where α is the fine structure constant.

II. RELATIVISTIC QUANTUM CHEMISTRY METHODS

In the hierarchy of physical models, a relativistic many-body theory to describe the electronic structure in atoms and molecules should be derived from a relativistic quantum field theory. The methods currently in use have been described as somewhat more *ad-hoc*.^{23,24} The state of the art has recently been reviewed again,^{23–28} and there are a number of textbooks available where detailed information on the topic can be found.^{29–34} Collections of expert articles on the topic of relativistic quantum theory for molecules have been edited, for instance, by Schwerdtfeger^{35,36} Hirao and Ishikawa,³⁷ Hess,³⁸ Kaldor and Wilson,³⁹ and Barysz and Ishikawa.⁴⁰ The latter collection contains articles aimed at non-specialists. Numerous older reviews are available as well; see Refs. 18 and 41–48 for a selection. We focus on the electronic motion and adopt the clamped nucleus approximation for brevity.

Saue²⁶ has pointed out that the level of relativistic treatment adds a third dimension to the usual way of assessing the quality of a model chemistry by the electron correlation level and the quality of the one-particle basis. At the lowest rung, there is the nonrelativistic treatment. Even with a complete basis and full correlation, the solution of the Schrödinger equation would give a poor description of a heavy-element system. In four-component (4c) relativistic quantum chemical methods, the Dirac one-electron Hamiltonian reads

$$h^D = c^2\beta' + c\boldsymbol{\alpha} \cdot \mathbf{p} + V = \begin{pmatrix} V & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & V - 2c^2 \end{pmatrix}, \quad (1)$$

where V is the external potential, $\boldsymbol{\sigma}$ is the vector of the 2×2 Pauli spin matrices, $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$, and \mathbf{p} is the momentum operator. Furthermore,

$$\beta' = \begin{pmatrix} 0_2 & 0_2 \\ 0_2 & -2 \cdot 1_2 \end{pmatrix}; \quad \boldsymbol{\alpha} = \begin{pmatrix} 0_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0_2 \end{pmatrix} \quad (2)$$

are representations of the 4×4 Dirac matrices expressed in terms of 2×2 sub-matrices. In (1), V and $V - 2c^2$ are to be multiplied by 1_2 which is the 2×2 unit matrix; this notation is implicit from here on. The zero of the energy scale E has been shifted to coincide with the electron rest mass energy (Fig. 1). The operator h^D acts on a 4-component spinor wavefunction which may describe an electron or a positron. The Hamiltonian goes back to Dirac who obtained a wave equation for spin-1/2 particles by linearizing and quantizing the relativistic energy expression of Sec. I with the help of a set of 4×4 matrices. Related to the block structure of h^D , the

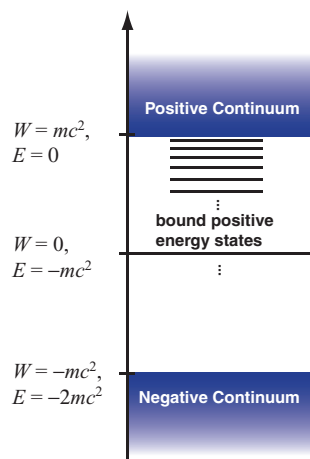


FIG. 1. Sketch of the continuum eigenvalue spectrum of the Dirac Hamiltonian. Also indicated are bound positive-energy states below $W = mc^2$, $E = 0$ which are the states that are of main concern in quantum chemistry. E is the energy scale adjusted to the electron rest-mass energy, conforming to the definition of h^D in Eq. (1).

wavefunction ψ^D is often written in terms of upper (“large”) and lower (“small”) 2-spinor components,

$$\psi^D = \begin{pmatrix} \psi^U \\ \psi^L \end{pmatrix}. \quad (3)$$

The Dirac one-electron operator (1) has positive and negative energy (W) solutions as indicated in Figure 1, with the discrete set of energies $W < mc^2$, $E < 0$ representing the sought-after bound electronic states of atoms and molecules. The operator h^D may be used in place of the nonrelativistic one-electron operator,

$$h^{\text{nel}} = \frac{1}{2} \mathbf{p} \cdot \mathbf{p} + V, \quad (4)$$

in electronic structure methods, for example, to realize a 4c Hartree-Fock calculation. By using methods known from non-relativistic correlated electronic structure theory, or alternatively via density functional theory (DFT), such a 4c method can then be extended to incorporate effects from electron correlation. There are a number of caveats related to the definition of the many-body Hamiltonian and the vacuum, as well as the role of negative-energy states; see, for instance, Refs. 23, 49, and 50.

A note on the lack of spin-dependence of the nonrelativistic one-electron operator (4) is in order. Spin arises naturally from Dirac’s theory, but in nonrelativistic theory it is introduced in an *ad-hoc* fashion. Realizing that $(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p}) = 1_2 \mathbf{p} \cdot \mathbf{p}$, a nonrelativistic Hamiltonian with spin may be written as

$$h^{\text{nel}} = \frac{1}{2} (\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p}) + V. \quad (5)$$

When magnetic fields are included in the Hamiltonian, there are a number of spin-dependent terms such as the spin Zeeman or the electron nucleus hyperfine operator that have a non-vanishing nonrelativistic limit. These can also be obtained by introducing the fields in Eq. (5), but not in Eq. (4).

When treating fields semi-classically, “minimal substitution”

$$\mathbf{p} \rightarrow \mathbf{p} - q\mathbf{A}; \quad E \rightarrow E - q\phi \quad (6)$$

allows for the inclusion of electric potentials ϕ and magnetic vector potentials \mathbf{A} in the equation for a particle with charge q . For an electron, $\mathbf{p} \rightarrow \mathbf{p} + \mathbf{A}$ in atomic units. In the one-electron Dirac Hamiltonian, this substitution gives the magnetic field dependent terms to be added to h^D as

$$h_{\text{mag}}^D = c\boldsymbol{\alpha} \cdot \mathbf{A}. \quad (7)$$

From the spin-dependent version of the nonrelativistic one-electron Hamiltonian one obtains instead the magnetic perturbation operators

$$h_{\text{mag}}^{\text{nel}} = \frac{1}{2} (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} + i\boldsymbol{\sigma} \cdot [\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p}] + A^2). \quad (8)$$

The nonrelativistic (and two-component relativistic) magnetic part of the Hamiltonian affords a “diamagnetic” term (proportional to A^2) which is not present in the 4c operator (7). In NMR calculations, for instance, the A^2 term gives rise to the diamagnetic shielding contribution when standard gauges for \mathbf{A} are employed. A diamagnetic contribution to a second-order derivative property such as NMR shielding or J -coupling is implicit in 4c theory. Such diamagnetic contributions were numerically traced back to terms involving negative energy eigenfunctions of h^D if one were to express the result in a sum-over-states expansion.⁵¹ The role of the negative energy states for diamagnetic shielding has also been emphasized by Pyykkö in early theoretical work on NMR chemical shifts.⁵² When a matrix formulation in a basis set, or suitable transformations at the operator level are employed, diamagnetic terms may appear explicitly in a 4c formalism.^{53–55} For additional references and further discussion, see also Refs. 56 and 57.

The nonrelativistic electron-electron (e - e) repulsion,

$$g(1, 2) = r_{12}^{-1}, \quad (9)$$

in the many-body electronic Hamiltonian $H = \sum_i h(i) + (1/2) \sum_{i \neq j} g(i, j)$ is an approximation in the relativistic domain since it represents an instantaneous interaction between two electrons neither taking into account the retardation effects from the finite speed of light nor magnetic interactions that arise in the equations from transforming the electrodynamic potentials between the reference frames of the electrons and nuclei. The aforementioned *ad-hoc* approach includes corrections to the e - e repulsion that were not rigorously derived from a higher-level many-body relativistic molecular quantum field theory but originate in the relativistic interaction between two classical charged particles subject to quantization using the relativistic velocity operator $c\boldsymbol{\alpha}$, to give in Coulomb gauge

$$g(1, 2) = \frac{1}{r_{12}} - \frac{\boldsymbol{\alpha}(1) \cdot \boldsymbol{\alpha}(2)}{r_{12}} + \frac{1}{2} \left[\frac{\boldsymbol{\alpha}(1) \cdot \boldsymbol{\alpha}(2)}{r_{12}} - \frac{(\boldsymbol{\alpha}(1) \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}(2) \cdot \mathbf{r}_{12})}{r_{12}^3} \right]. \quad (10)$$

The first correction term is a magnetic interaction known as the Gaunt term, and the sum of the Gaunt term and the

operator in brackets is the (frequency-independent) Breit term. The Breit operator may be considered as an approximation of the quantum electro-dynamics (QED) correction to the interaction between two electrons.⁵⁸ There is a more general frequency-dependent version, where the frequencies correspond to differences in the energies of plane waves used to represent the e - e interaction. In conjunction with \hbar^D for the one-electron part, the resulting Hamiltonian is the Dirac-Coulomb-Breit (DCB) Hamiltonian and serves as a common starting point from which practical correlated electronic structure methods can be implemented. Additional QED based perturbative corrections $\mathcal{O}(c^{-3})$ may be added to the operator. There has been some debate whether these and/or the Breit term^{41,59,60} may be used in variational calculations or if their effects must only be evaluated via perturbation theory. In order to account for effects due to the Breit term on atomic and molecular properties other than total energies and orbital energies, a variational treatment would be preferred.⁵⁹ Although the DCB Hamiltonian is in general not Lorentz-invariant, it has been said to provide “an excellent approximation to the full theory.”⁴⁶ There are, however, important conceptual issues connected with the DCB Hamiltonian and the role of the vacuum in correlated relativistic quantum chemical methods that need to be addressed in future work.^{23,49} Effects beyond DCB lie in the realm of QED which are discussed at some length in a recent review.²⁵

The pairs of upper and lower components in Eq. (3) are not independent from each other. Consider the Dirac equation $\hbar^D \psi^D = \psi^D E$ for a one-electron system. A separation of the equations for each 2×2 sub-block gives

$$\psi^L = X \psi^U \quad \text{with} \quad X = \frac{1}{2c} k \boldsymbol{\sigma} \cdot \mathbf{p}, \quad (11)$$

where

$$k = \left(1 - \frac{V - E}{2c^2}\right)^{-1}. \quad (12)$$

The c^{-1} factor in Eq. (11) is the reason for calling ψ^L the small component. For positive-energy solutions, it is typically much smaller than ψ^U , hence the name is justified. (It may happen that ψ^L is larger than ψ^U . An example would be a hydrogen-like $p_{1/2}$ orbital for high Z very close to the nucleus.) If the relation (11) between the upper and lower components is not enforced as a constraint this will lead to serious problems in variational calculations of 4c wavefunctions as one attempts to saturate the basis set.⁶¹ In the nonrelativistic limit,⁶² $X = \frac{1}{2c} \boldsymbol{\sigma} \cdot \mathbf{p}$. Experience has shown that when using a basis $\{\chi\}$ for the upper components and a basis for the lower components that includes $\{\boldsymbol{\sigma} \cdot \mathbf{p} \chi\}$ a variational collapse can be kept under control. This is referred to as “kinetic balance.”⁶³ Restricting the lower-component basis set to only $\{\boldsymbol{\sigma} \cdot \mathbf{p} \chi\}$ means restricted kinetic balance (RKB) which, however, allows the wavefunction coefficients for the upper and lower components to be different (they become proportional in the nonrelativistic limit). Unless the upper component basis set has sufficient flexibility such that the set of functions $\{\boldsymbol{\sigma} \cdot \mathbf{p} \chi\}$ can describe the lower components well enough, RKB may represent a restriction. As can be seen from Eq. (11), the additional factor of k in the relation

requires flexibility in the lower-component basis in particular in the atomic cores where k may differ significantly from unity. Within an unrestricted kinetic balance (UKB) scheme, one tries to make the lower-component basis more flexible while keeping the important $\{\boldsymbol{\sigma} \cdot \mathbf{p} \chi\}$ functions from a basis designed to describe the upper components well enough. Liu has strongly advocated in favor of RKB and abandoning UKB, providing a number of reasons.²⁴ The construction of exact two-component Hamiltonians (see below) is also facilitated by the use of RKB. For further discussion of these and additional kinetic balance schemes, see Ref. 64.

Equation (11) allows for the elimination of the small component (ESC) from the Dirac equation, yielding a pseudo eigenvalue equation for an electron in terms of the upper components alone,

$$h^{\text{ESC}} \psi^U = \left[V + \frac{1}{2} (\boldsymbol{\sigma} \cdot \mathbf{p}) k (\boldsymbol{\sigma} \cdot \mathbf{p}) \right] \psi^U = \psi^U E. \quad (13)$$

This indicates that, in principle, it is possible to perform calculations with either ψ^U or ψ^L alone in a two-component (2c) relativistic framework. As written, ψ^U in Eq. (13) is identical to ψ^U in Eq. (3) and not normalized since ψ^D is supposed to be normalized: $1 = \langle \psi^D | \psi^D \rangle = \langle \psi^U | 1 + X^\dagger X | \psi^U \rangle$ with X defined in Eq. (11). Accordingly, a re-normalized upper component is obtained via

$$\sqrt{1 + X^\dagger X} \psi^U. \quad (14)$$

One should keep in mind that $\sqrt{1 + X^\dagger X}$ is not simply a normalization factor but an operator that changes the shape of ψ^U . Consider a one-electron system. The 4c electron charge density $\rho(\mathbf{r}) = \psi^{D*} \psi^D$ involves both the upper and the lower components. Therefore, $\rho'(\mathbf{r}) = \langle \psi^U | \psi^U \rangle^{-1} \psi^{U*} \psi^U$ cannot be the same as the electron charge density. This is referred to as *picture change*. The 2c density $\rho'(\mathbf{r})$ has been associated with the position of the electron mass.^{65,66} In order to calculate the charge density from ψ^U , the position operator needs to be transformed as discussed below, or a 4c charge density needs to be reconstructed with the help of Eq. (11). From the factor k in Eq. (11) it is seen that the lower components are significant where $V - E$ is comparable to, or larger than, $2c^2$ which is typically the case near the nuclei where V is very large in magnitude, and for deep core states in heavy element systems where E can also be very large in magnitude. Figure 2 shows the relativistic change of order c^{-2} for the radial density of the hydrogen atom $2p_{1/2}$ state according to 4c and 2c theory.⁶⁷ The relativistic contraction is readily apparent, and so is the difference between $\rho(r)$ and $\rho'(r)$ in particular at smaller r . Picture-change effects are less pronounced in the valence regions and therefore less of a concern when calculating dipole and higher multipole moments. For properties such as electric field gradients (EFGs) which depend on polarizations not only in the valence but also in (outer) atomic core shells, picture-change effects can be pronounced.^{68–70} Additional examples are discussed in Sec. III.

Equation (13) is not practical since the operator, via k , depends on E . More formally, one may seek a transformation of a 4c Hamiltonian, written below as a more general many-electron operator (e.g., the DCB Fock operator) with a 2×2

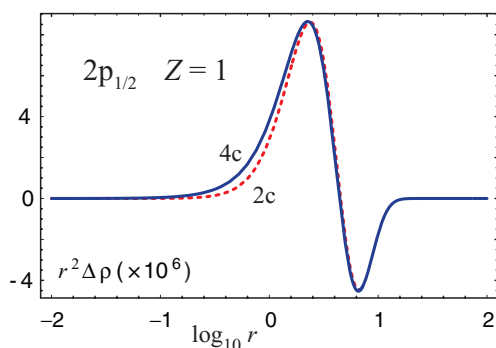


FIG. 2. Relativistic change $r^2 \Delta \rho$ of the radial density of the hydrogen atom $2p_{1/2}$ state (point nucleus) calculated with two-component (dashed) and four-component (solid line) relativistic theory correct to order c^{-2} ; see Ref. 67.

block structure,

$$U^\dagger h^D U = U^\dagger \begin{pmatrix} h^{UU} & h^{UL} \\ h^{LU} & h^{LL} \end{pmatrix} U = \begin{pmatrix} h^{UU} & 0 \\ 0 & h^{LL} \end{pmatrix}, \quad (15)$$

in order to decouple the equations for ψ^U and ψ^L (Foldy-Wouthuysen (FW) transformation⁶⁶) and renormalize ψ^U . The charge density, for instance, can then be calculated as $\rho'(\mathbf{r}')$ by transforming the position operator as $\mathbf{r}' = U^\dagger \mathbf{r} U$ instead of explicitly reconstructing the 4c density. Likewise, for calculations of expectation values and response properties the operators of other physical observables need to be transformed as $\hat{A}' = U^\dagger \hat{A} U$ where \hat{A} is the correct operator for the 4c case. This is another example of a picture change. The discussion follows Ref. 26: The transformation U can be written as a product of a decoupling step U^d and a renormalization step U^N without the explicit energy dependence of the ESC equation (13), as^{26,71,72}

$$U = U^d U^N = \begin{pmatrix} 1 & -X^\dagger \\ X & 1 \end{pmatrix} \begin{pmatrix} \mathcal{N}^+ & 0 \\ 0 & \mathcal{N}^- \end{pmatrix}, \quad (16)$$

where $\mathcal{N}^+ = 1/\sqrt{1+X^\dagger X}$ and $\mathcal{N}^- = 1/\sqrt{1+XX^\dagger}$ arise from the renormalization of ψ^U and ψ^L in the decoupled equations. One can show⁷² that an operator X that gives a block-diagonal Hamiltonian from $U^\dagger h^D U$ satisfies

$$2c^2 X = c\boldsymbol{\sigma} \cdot \mathbf{p} - [X, V] - Xc\boldsymbol{\sigma} \cdot \mathbf{p}X. \quad (17)$$

Including the normalization step, the wavefunction transforms as

$$U^\dagger \psi^D = \begin{pmatrix} \mathcal{N}^+(\psi^U + X^\dagger \psi^L) \\ \mathcal{N}^-(\psi^L - X\psi^U) \end{pmatrix}. \quad (18)$$

For the sought-after positive-energy electronic states, one then demands that the lower components of $U^\dagger \psi^D$ vanish, which requires $\psi^L = X\psi^U$, as in Eq. (11). The upper component of $U^\dagger \psi^D$ then becomes the function in Eq. (14).

Much activity has been directed in recent years at the development of practical and efficient methods to construct a fully decoupled 2c one-electron Hamiltonian from matrix representations of the 4c Hamiltonian,^{73–77} allowing for a full elimination of the lower components with explicit construction of a matrix representation of U . Information regarding

the development of these methods, now collectively termed X2C (“eXact 2-Component”), and details about the construction of such operators, can be found in Refs. 24 and 26. In this context, we also mention elimination schemes dubbed IOTC to construct two-component relativistic operators by Barysz and co-workers^{78–81} and normalized elimination of the small component (NESC) methods^{82,83} which have helped paving the way for the development of X2C. There is no closed-form expression available for the X2C one-electron Hamiltonian, but its approximate construction in matrix form utilizing a finite basis set can be summarized in a few algorithmic steps, none of which require the calculation of molecular integrals that are not already available in 4c codes.²⁶ The construction of U in matrix form requires the solution of the 4c equations first; the transformation matrix is then obtained from the relation between the wavefunction coefficients between the upper and the lower components. As such, the X2C Hamiltonian is as complex as the 4c Hamiltonian since knowledge of the latter is required to construct the former. An advantage of using X2C instead of 4c can be expected in correlated relativistic wavefunction methods where the computational effort is dominated by calculations and transformations of two-electron integrals and a transformation of the one-electron part of the Hamiltonian to 2c form may lead to significant computational savings. An approximate form of the relation between the upper and lower components is already known. From Eq. (11), $X \approx (2c)^{-1} \boldsymbol{\sigma} \cdot \mathbf{p}$. Deviations from the exact relations are significant mainly deep in the atomic cores, and therefore favorably scaling atoms-in-molecules concepts can be employed in order to render the calculation more efficient.²⁴ Further, these approaches may be combined with 4c matrix formulations for magnetic properties.^{84–86} For spin-free (scalar relativistic) X2C and NESC, analytic methods for calculations of nuclear gradients and second derivatives have been reported.^{87–89}

Regarding magnetic properties such as NMR shielding, the concept of “magnetic balance”⁵¹ becomes important: The lower-component basis set should not only contain $\{\boldsymbol{\sigma} \cdot \mathbf{p}\chi\}$ functions, but also $\{\boldsymbol{\sigma} \cdot \mathbf{A}\chi\}$ (see Eq. (6) (Ref. 90)). Implementations of 4c NMR shielding tensor calculations with restricted magnetic balance have been reported not long ago,^{86,91,92} including extensions to using gauge-including (magnetic-field dependent) basis functions.^{86,92} Olejniczak *et al.* recently reported a simplified magnetic balance scheme for 4c NMR calculations whereby the flexibility of unrestricted magnetic balance can be combined with the advantages of a restricted magnetic balance formalism.⁹³

Quasi-relativistic two-component Hamiltonians are approximate 2c operators where the decoupling of Eq. (15) is achieved in an approximate, incomplete, way. In order c^{-2} , the Pauli operator is obtained from the one-electron part of the DCB Hamiltonian. When the two-electron terms of $\mathcal{O}(c^{-2})$ are included, the operator is referred to as the Breit-Pauli Hamiltonian. In the field-free case, the one-electron part reads

$$h^{\text{Pauli}} = h^{\text{nr}} - \frac{\mathbf{p}^4}{8c^2} - \frac{(\mathbf{p}^2 V)}{8c^2} + \frac{i}{4c^2} \boldsymbol{\sigma} \cdot [(\mathbf{p}V) \times \mathbf{p}]. \quad (19)$$

For a list of operators, including some important two-electron terms, that arise in the presence of magnetic fields see, for

example, Refs. 29 and 94. The first of the relativistic correction terms in Eq. (19) is seen to be a quantized form of the p^4 correction of the kinetic energy discussed in Sec. I, which is usually termed the mass-velocity correction (MV) and associated with the relativistic mass increase of the electron. The second term of $\mathcal{O}(c^{-2})$ is the one-electron Darwin term (Dar) associated with the “Zitterbewegung” of the electron in areas where the potential is strong enough to create electron-positron pairs.²⁶ The last term on the right-hand side of Eq. (19) is the SO coupling operator. The Pauli operator is not variationally stable and creates diverging perturbation terms in $\mathcal{O}(c^{-4})$ and higher^{95,96} (in low order they can be grouped to arrive at a non-singular result for hydrogen-like atoms, but these terms would be very tricky to handle numerically in many-electron codes). Its use is therefore deprecated, although much work has been put into calculations of all relevant Breit-Pauli magnetic perturbation operators until not long ago.^{97–99} The large number of operators obtained in order c^{-2} , some of which are not suitable for calculations due to their singular nature, renders variational methods with other quasi-relativistic operators more convenient.

A variationally stable quasi-relativistic operator that is presently in widespread use is obtained by rewriting k in Eq. (13) as

$$k = \left(1 - \frac{V - E}{2c^2}\right)^{-1} = \frac{2c^2}{2c^2 - V} \left(1 + \frac{E}{2c^2 - V}\right)^{-1} \quad (20)$$

and expanding the term in parentheses in a power series in $E/(2c^2 - V)$. The zeroth-order regular approximation (ZORA) Hamiltonian^{100,101} represents the zeroth-order term of this expansion, yielding either directly from Eq. (13), or from Eq. (16) with $X \approx \frac{1}{2c} \frac{2c^2}{2c^2 - V} \boldsymbol{\sigma} \cdot \mathbf{p}$ and $\mathcal{N}^+ = \mathcal{N}^- \approx 1$, the operator

$$H_{\text{ZORA}} = V + \frac{1}{2}(\boldsymbol{\sigma} \cdot \mathbf{p})\mathcal{K}(\boldsymbol{\sigma} \cdot \mathbf{p}) \quad (21a)$$

$$= V + \frac{1}{2}\mathbf{p} \cdot \mathcal{K}\mathbf{p} + \frac{i}{2}\boldsymbol{\sigma} \cdot [\mathbf{p}\mathcal{K} \times \mathbf{p}], \quad (21b)$$

where

$$\mathcal{K} = \frac{2c^2}{2c^2 - V} = \frac{1}{1 - V/(2c^2)}. \quad (22)$$

The nonrelativistic limit is obtained via $\mathcal{K} \rightarrow 1$, $\mathbf{p}\mathcal{K} \rightarrow 0$. The relation to the Pauli operator is furnished by $\mathcal{K} \approx 1 + V/(2c^2)$ for $V \ll 2c^2$. The ZORA and Pauli spin-orbit operators become identical in this case. The spin-free c^{-2} one-electron energy correction in first-order perturbation theory from ZORA for small V is $(1/2)\langle\psi^{\text{nr}}|\mathbf{p} \cdot \mathcal{K}\mathbf{p}|\psi^{\text{nr}}\rangle \approx T^{\text{nr}} + (1/4c^2)\langle\psi^{\text{nr}}|\mathbf{p} \cdot V\mathbf{p}|\psi^{\text{nr}}\rangle$. With V replaced by $V - E$, the expectation value on the right would equate to the sum of the Pauli MV and Dar terms. The operators (19) and (21) differ substantially in the atomic cores where V is large and where the large potential leads to the breakdown of the Pauli operator in terms of variational stability but \mathcal{K} serves to regularize the Hamiltonian.¹⁰² The ZORA operator is not invariant with respect to a change in the origin of the energy scale (gauge dependency), via V in \mathcal{K} of Eq. (22), such that $V + \Delta$ would not give the correct value $E + \Delta$ for the resulting energy. Most of the

available implementations make use of model potentials in \mathcal{K} (sum of atomic potentials or the potential from a sum of atomic densities plus the sum of nuclear potentials),^{103–105} which alleviate this problem. Likewise, a “scaled ZORA” approach designed to match ZORA with 4c eigenvalues for one-electron systems¹⁰⁶ eliminates most of the gauge-dependency errors and gives greatly improved energies for core orbitals in heavy atoms. With $X \approx X_0 = \frac{1}{2c} \frac{2c^2}{2c^2 - V} \boldsymbol{\sigma} \cdot \mathbf{p}$ and $\mathcal{N}^+ \approx 1 - \frac{1}{2}X_0^\dagger X_0$, $\mathcal{N}^- \approx 1 - \frac{1}{2}X_0 X_0^\dagger$, one obtains a first-order regular approximation; the corresponding working expressions have been used to derive the scaled-ZORA equations more rigorously. Along the same lines, Dyall and van Lenthe¹⁰⁷ introduced an infinite-order regular approximation (IORA) which takes the ZORA approximation for X fully into account in the square roots in $U^{\mathcal{N}}$ of Eq. (16). IORA is not the same as an infinite-order expansion of Eq. (20). However, unlike ZORA, the IORA Hamiltonian includes all relativistic terms in order c^{-2} in addition to some higher order terms, and a simple expression to eliminate picture change effects in order c^{-2} is available.¹⁰⁷ A nice feature of the ZORA operator is that it is straightforward to derive magnetic perturbation terms from it at the operator level.^{21,108} For a given vector potential,

$$h_{\text{mag}}^{\text{ZORA}} = \frac{1}{2}([\mathbf{p} \cdot \mathcal{K}\mathbf{A} + \mathbf{A}\mathcal{K} \cdot \mathbf{p}] + i\boldsymbol{\sigma} \cdot [\mathbf{p} \times (\mathcal{K}\mathbf{A}) + (\mathbf{A}\mathcal{K}) \times \mathbf{p}] + \mathcal{K}\mathbf{A}^2). \quad (23)$$

The nonrelativistic limit (8) is obtained via $\mathcal{K} \rightarrow 1$.

Another quasi-relativistic Hamiltonian that has found wide-spread use^{109,110} is the Douglas-Kroll-Hess (DKH) Hamiltonian which is constructed via a sequence of transformations $U = U_0 U_1 U_2 \dots$ in orders of the potential V . For a free particle, the FW transformation to block-diagonal form can be written in closed form. When the free-particle FW transformation is applied to the Dirac Hamiltonian with an external potential, one obtains²⁶

$$U_0^\dagger h^D U_0 = \begin{pmatrix} E_p - c^2 & 0 \\ 0 & -E_p - c^2 \end{pmatrix} + \begin{pmatrix} K(V + RVR)K & K[R, V]K \\ -K[R, V]K & K(V + RVR)K \end{pmatrix} \quad (24)$$

with

$$E_p = \sqrt{\mathbf{p}^2 c^2 + c^4}; \quad K = \sqrt{\frac{E_p + c^2}{2E_p}},$$

$$R = R'\boldsymbol{\sigma} \cdot \mathbf{p}; \quad R' = \frac{c}{E_p + c^2}. \quad (25)$$

For $V = 0$, the Hamiltonian is indeed block diagonal and represents a quantized version of the relativistic classical free particle energy. The DKH sequence for a molecular Hamiltonian starts with a free-particle FW transformation U_0 (DKH0) and subsequently decouples the upper and lower components of the second term on the right-hand side of Eq. (24) in the DKH1, DKH2, ... sequence. Hess and co-workers found a practical way to achieve the decoupling by formulating the operators in a basis set that diagonalizes \mathbf{p}^2 in order to arrive at a convenient formulation.^{111–113} Similar techniques have

also been used for the RESC method developed by Nakajima and Hirao.¹¹⁴ The construction of the DKH operator has been pushed essentially to arbitrary order.^{115,116} A comparison between different scalar relativistic decoupled two-component methods (DKH, BSS, and X2C) has recently been made in Ref. 117. Not surprisingly, the different methods work equally well, with comparable computational effort. An important issue is the inclusion of the two-electron potential in the transformations; without doing so picture-change errors arise.

The subsequent introduction of magnetic-field dependent terms in the DKH method in a rigorous way has taken a rather long time and the efforts of several research groups.^{57,118–122} At the DKH1 level, the expression for the magnetic perturbation operator is relatively compact and may be written as¹²⁰

$$h_{\text{mag}}^{\text{DKH1}} = c(K[R'\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}R']K + i\boldsymbol{\sigma} \cdot \mathbf{K}[R'\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p}R']K). \quad (26)$$

The structure of the paramagnetic (linear in \mathbf{A}) terms is not unlike ZORA in the sense that it resembles the nonrelativistic expression but with additional kinematic factors that account for relativistic effects. The nonrelativistic limit ($K \rightarrow 1$, $R' \rightarrow (2c)^{-1}$) recovers the terms from Eq. (8) that are linear in \mathbf{A} . A “diamagnetic” term proportional to \mathbf{A}^2 as in the nonrelativistic and ZORA schemes appears in the next order, DKH2. Additional significant efforts have been directed at avoiding picture-change effects in molecular property calculations. The transformation U is not constructed explicitly in DKH codes, and therefore care needs to be taken that the matrix elements for electric field perturbation operators, for instance, are properly transformed as well.^{70,123}

A relativistic perturbation theory that avoids the infinities of the Breit-Pauli Hamiltonian in higher orders is the so-called “direct” or “Dirac” four-component perturbation theory (DPT). Following a change of metric between upper and lower components in the Dirac-equation, an expansion of the resulting four-component equation in powers of c^{-2} is straightforward and leads to non-singular first- and higher order expressions for the energy and the wavefunction.^{124–126} A treatment of magnetic properties within the DPT framework has been formulated.⁹⁰ For an implementation of magnetic properties see, for instance, Ref. 127.

As an alternative to direct relativistic methods that consider special relativity directly in the Hamiltonian, relativistic effective core potentials (RECPs) provide a way to incorporate relativistic effects in molecular computations. We will not discuss such pseudopotential methods in detail herein but focus on direct relativistic methods that are suitable for all-electron calculations. See a recent review by Dolg and Cao¹²⁸ on RECPs for details and references to original articles. Consideration of spin-orbit coupling is also possible in these methods. Extensive benchmark calculations have shown that RECPs can yield reliable properties of heavy element compounds. For molecular properties where the core tails of the valence orbitals are not of concern, pseudopotentials are also straightforward to apply, albeit with some caution as far as magnetic properties and distributed gauge origin methods are concerned.¹²⁹ For properties such as NMR shifts or spin-spin coupling the all-electron electronic structure near

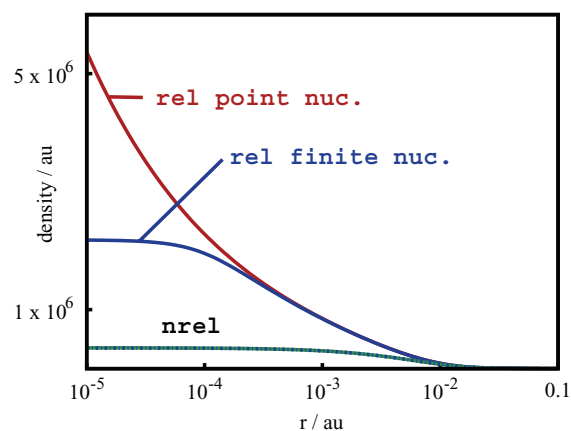


FIG. 3. Electron charge density of the gold atom as a function of the electron-nucleus distance r , for small radii. Four-component relativistic numerical DFT calculations ($X\alpha$ functional) with a point nucleus and with a finite Gaussian nucleus model.¹⁹⁰ Nonrelativistic results were obtained by scaling the speed of light by a factor of 10^5 (nrel, point and finite nucleus data are indistinguishable on the scale of the plot). The effective nuclear radius used for the finite nucleus calculations was 1.03×10^{-4} .

the nuclei is important and needs to be reconstructed if one attempts to calculate such properties within a pseudopotential method.^{130,131}

III. EXAMPLES OF RELATIVISTIC EFFECTS

One may distinguish between relativistic effects at the one-electron level and those specific to many-electron systems. At the one-electron level, there are the modifications to the kinetic and potential energy operators, and SO coupling induced by the nuclear potential(s). The e - e potential interactions in many-electron systems give rise to additional relativistic effects. Some of these resemble the one-electron terms, with the nuclear potential replaced by the electronic Coulomb potential. Examples are the two-electron Darwin and the two-electron SO operators arising in the Breit-Pauli Hamiltonian. Additional terms arise from magnetic interactions between two electrons, such as the spin-other-orbit term. For a full account of these operators in order c^{-2} see Refs. 29, 41, and 132.

A. Atomic orbitals

For one-electron (hydrogen like) atoms, all orbitals are relativistically stabilized and contracted. These effects are largest for $s_{1/2}$ and $p_{1/2}$ and decrease with increasing principal quantum number as well as with increasing angular momentum. In nonrelativistic theory, s orbitals adopt finite values at the nuclei and all other types of radial functions go to zero for $r \rightarrow 0$ (point nuclei). For point nuclei, the relativistic $s_{1/2}$ and $p_{1/2}$ radial orbital functions have weak negative-exponent divergences at the nucleus. Higher angular momenta afford non-divergent radial functions whose derivatives have weak negative-exponent divergences. With finite nuclei,¹³³ there are no divergent terms. Qualitatively, these near-nucleus features occur also in many-electron atoms. For large Z , there are very pronounced differences between relativistic and nonrelativistic calculations in particular for small electron-nucleus distances. Figure 3 shows as an example the near-nucleus

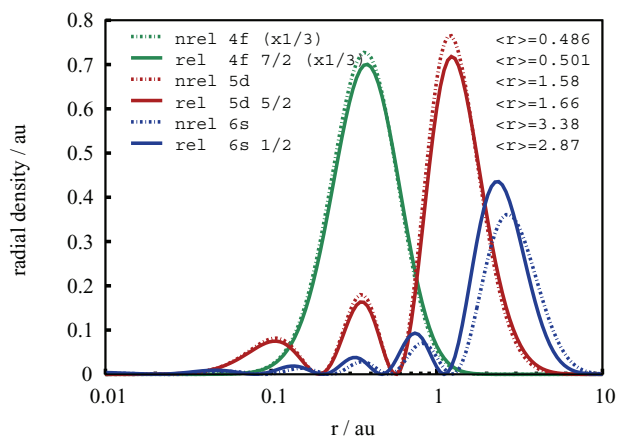


FIG. 4. Radial densities of selected valence orbitals of the gold atom. $6s$ contracts relativistically, while $5d_{5/2}$ and the $4f$ orbitals expand due to indirect effects. Four-component numerical DFT calculations (X α functional) with Gaussian nucleus model. Nonrelativistic results were obtained by scaling the speed of light by a factor of 10^5 . The density of the relativistic $5d_{3/2}$ orbital (not shown, $\langle r \rangle = 1.57$) closely resembles that of the nonrelativistic calculation.

behavior of the electron density of the gold atom. At the scale of the plot, the difference between the nonrelativistic point and finite nucleus calculations is not visible. For the relativistic calculations, the finite-nucleus effects on the density becomes noticeable for radii below 10^{-3} and very large for radii less than the effective nuclear radius (about 10^{-4}). Although finite nucleus effects are not by definition “relativistic,” they tend to be large only in relativistic calculations. The pronounced increase of the electron density in the K-shell and near the nucleus due to relativistic effects is evident from the plots, both for the finite nucleus and for the point-nucleus calculation. It is therefore not surprising that there are very large relativistic effects on properties such as electron nucleus hyperfine coupling or NMR parameters (in particular J -coupling) for heavy elements. One must keep in mind that some of the density increase originates from the relativistic effects on the tails of the outer core and valence orbitals close to the nucleus and in the K-shell, in particular from $s_{1/2}$

and $p_{1/2}$ orbitals. Thus, genuine chemical properties that are dominated by the valence orbitals may exhibit large relativistic effects originating from the inner core regions of heavy atoms.

In self-consistent calculations of many-electron systems there are additional relativistic effects arising from the self-consistency. These changes have been termed “indirect” effects⁸ in order to distinguish them from the direct kinematic effects on the electronic structure arising from the presence of the relativistic modifications in the Hamiltonian. For instance, because $s_{1/2}$ and $p_{1/2}$ orbitals tend to contract most strongly due to relativistic effects, orbitals in the same shell but with higher angular momentum experience a concomitant relativistically increased screening of the nucleus. In self-consistent calculations, the net effect is a relativistic destabilization and expansion of $d_{5/2}$ and orbitals with higher j . For $p_{3/2}$ and $d_{3/2}$ the direct stabilization and contraction, and the indirect destabilization and expansion, tend to cancel to some degree, and the final sign of the effect is not particular systematic. Representative examples are shown in Figure 4 for the gold atom. We point, in particular, to the large relativistic contraction of the $6s$ orbital, reducing $\langle r \rangle$ from 3.4 to 2.9 bohrs which is predominantly a result of direct relativistic effects, and the indirect relativistic expansions of orbitals in inner shells with higher angular momentum.

For a given orbital expectation value y such as energy, radial expectation values, momentum, kinetic, and potential energy, and others, one may define a relativistic correction factor γ , such that $y^{\text{rel}} = y^{\text{nrel}}[1 + \gamma_y(Z/c)^2]$ which allows studying periodic trends more easily among atoms with very different Z (keeping in mind that γ itself contains relativistic corrections of $\mathcal{O}(c^{-2})$). When plotted for the $s_{1/2}$ orbital energies and the orbital radii in many-electron atoms, as shown in Figure 5, a pronounced maximum is observed at $Z = 79$ for the $6s$ orbital. This is the celebrated *gold maximum* of relativistic effects. The gold maximum arises from a variety of factors, among those the lanthanide contraction and the filled $5d$ shell in combination with the $6s^1$ configuration. Indirect effects amplify the $6s$ contraction in Au. If the third transition

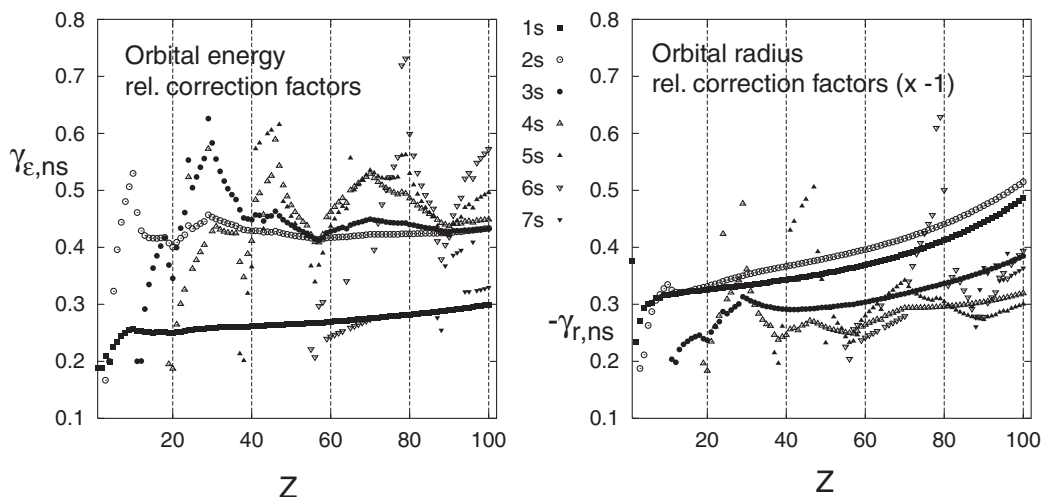


FIG. 5. Relativistic correction factors γ (see text) for energies ϵ and radii r of $s_{1/2}$ orbitals neutral many-electron atoms. Figure generated from four-component HF data reported by Desclaux, Ref. 191.

metal row had systematic $6s^2$ configurations, the maximum of relativistic effects in the period for the valence s orbital would occur for Hg. For additional details and an investigation of the periodic trends of various relativistic orbital correction factors see Ref. 134.

Given the relativistic effects on s and p orbital radii, it is not surprising that effective radii of atoms, particularly in groups 1, 2, 11–14, but also in other groups, shrink due to relativity, leading to a reversal of the trend of increasing atomic radii when going down a group in the periodic table. For instance, because of the large relativistic contraction of the gold valence shell, the radius of the gold atom is somewhat smaller than that of silver when calculated relativistically. In nonrelativistic calculations, the “normal” periodic trend of increasing radius with increasing atom number is obtained instead in group 11. Regarding the similarity between Zr and Hf, it was found that it is caused by a near-perfect cancellation of shell-structure and relativistic trends.¹³⁵ About 10% of the lanthanide contraction may be attributed to relativity. For details and further examples, see Pyykkö.¹⁸ Along with the significant relativistic orbital contractions and expansions occurring in the heavy-atomic part of the periodic table, there are changes in the atomic shell structures which have been studied recently by relativistic MCSCF calculations with the help of topological analyses of the electron densities.¹³⁶ Topological analyses of relativistic electron density changes in transition metal complexes $M(C_2H_2)$ with $M = Ni, Pd, Pt$, have also been reported.¹³⁷

B. Bond distances in molecules

Considering the relativistic contraction of s and $p_{1/2}$ shells in heavy atoms, one may expect that atomic distances in many molecules with heavy atoms shrink relativistically as well,⁴² and that chemical bonds are shorter when calculated with a relativistic formalism. Accordingly, one would expect nonrelativistic calculations to overestimate interatomic distances involving heavy elements. This is indeed found often; cases of relativistic bond length expansions appear to be rare.¹⁸ Among the molecules that exhibit pronounced bond length contractions (on the order of 0.2 to 0.3 Å depending on the type of calculation) are the diatomics AuH and Au₂. Due to their small size these molecules have been studied extensively by theory. One may ask the question whether the radial extension of free atoms, and relativistic effects thereupon, has any bearing on the relativistic chemical bond contraction in molecules. One may refer to the atomic contraction as a promolecular effect. Therefore, the question is whether the bond length contraction is a promolecular effect. To first order in c^{-2} , the unintuitive answer is apparently “no.”^{138,139} In order to arrive at this result, consider the first-order (in c^{-2}) relativistic correction of the energy, $E^{(1)} = \langle \Psi^{(0)} | H^{(1)} | \Psi^{(0)} \rangle$, where $H^{(1)}$ is the relativistic correction to the Hamiltonian of order c^{-2} and $\Psi^{(0)}$ is the nonrelativistic wavefunction. Relativistically corrected potential curves $E(R) = E^{(0)}(R) + c^{-2}E^{(1)}(R)$ for AuH and Au₂, for instance, where R is the interatomic distance produce the bulk of the relativistic corrections of the equilibrium bond length R_e . Since $\Psi^{(0)}$ does not contain any information about the promolecular relativistic effects the

conclusion must be that in leading relativistic order the minimum of $E(R)$ is unrelated to the relativistic effects in the promolecule.

There is a different way to look at this problem.¹⁴⁰ A relativistic bond contraction or expansion is driven by a non-vanishing relativistic contribution to the intramolecular force $F = -dE/dR$ at the nonrelativistic equilibrium distance (with $F^{\text{nr}} = 0$). In other words, one needs to consider $F^{(1)} = -dE^{(1)}/dR$. Differentiating $E^{(1)} = \langle \Psi^{(0)} | H^{(1)} | \Psi^{(0)} \rangle$ with respect to R gives a term involving $\partial \Psi^{(0)} / \partial R$ as well as one with $\Psi^{(0)}$ exclusively, and there is still no promolecular relativistic contribution. But the order of differentiation can be switched, $dE^{(1)}/dR = d^2E/dRdc^{-2}$ where one first calculates dE/dR and then takes the leading relativistic correction of the force. One term of the resulting expression is the Hellmann-Feynman electrostatic force calculated with $\rho^{(1)}$, the electron density change in order c^{-2} . The density change $\rho^{(1)} = \rho^{(1)\text{pro}} + \Delta\rho^{(1)}$ contains the promolecular relativistic density change $\rho^{(1)\text{pro}}$ and the relativistic change of the deformation density $\Delta\rho^{(1)}$. For AuH, Au₂, and selected other examples, it was found that the promolecular contribution is not dominant and that in this alternative calculation scheme the main relativistic contribution to the binding force comes from the relativistic effects on the deformation density.^{94,141} Therefore, the two ways of analyzing the bond length effects lead to comparable conclusions: The relativistic bond length contractions (and rare cases of expansions) are predominantly caused by relativistic effects on the molecular deformation density, and atomic relativistic contractions or expansions play only a secondary role.

C. Gold, mercury, lead, U₂

In the introduction we have pointed toward several iconic examples of relativistic effects. The first three are related to the exceptional relativistic stabilization of the $6s$ orbital around the end of the third transition metal series. The fact that Hg is the only metal that is liquid at room temperature has long been attributed to relativistic effects.^{41,142} The strong relativistic stabilization and contraction of the Hg $6s$ shell and the atom's closed-shell nature render Hg hard to polarize and chemically relatively inert. It is indeed very likely that the low melting point of Hg metal, -39°C , is heavily affected by relativity. For comparison, the melting point of Cd metal, which may be regarded as “nonrelativistic mercury,” is 321°C . A direct proof by comparing *ab-initio* relativistic and nonrelativistic calculations of the melting point of large Hg clusters appears to be forthcoming, based on recent developments of Hg interatomic potentials.¹⁴³ The yellow color of solid gold has for a long time been attributed to relativistic effects.¹⁸ For the atom, the relativistic stabilization of the $6s$ orbitals and the destabilization of the $5d$ level decreases the gap between the atomic orbital levels as compared to silver. In the solid, this translates to a concomitant onset of an absorption in the visible region, around 2.4 eV, in the reflexivity spectra¹⁴⁴ which was assigned to a transition from the $5d$ to the $6s$ band.¹⁴⁵ For silver metal, the corresponding absorption does not occur until 3.7 eV which is already in the ultraviolet.¹⁴⁴ Regarding the origin of the very large relativistic contribution to the

TABLE I. Dissociation energy D_0 of dihydrogen (cm^{-1}).

Calculation	Theory	Expt.
H ₂ , Kołos and Wolniewicz 1964–1968 ^a	36 117.4	36 118.3(4)
Bunker, 1969 ^b	36 117.9	
H ₂ ^c	36 118.069 5(10)	36 118.069 62(37)
D ₂ ^d	36 748.363 3(9)	36 748.362 86(68)

^aCalculation: Ref. 11. Experiment: Ref. 192.^bAs reported in Ref. 192.^cCalculation: Jeziorski *et al.*, Ref. 146. Experiment: Ref. 147.^dCalculation: Jeziorski *et al.*, Ref. 146. Experiment: Ref. 148.

lead - acid battery voltage,⁶ most of the effect has been traced back to the oxidative power of solid PbO₂ which, in turn, is related to the particular stabilization of the unoccupied Pb 6s levels in the solid due to relativistic effects. Regarding the quintuple bond in U₂, Gagliardi and Roos noted in their article that, based on their spin-orbit CASPT2 calculations, U₂ affords three fully developed electron-pair bonds, one σ and two π , with the latter formed by combinations of 6d and 5f uranium orbitals.⁵ Relativistic effects are in part responsible for less pronounced atomic shell structures in heavy elements, and the 6d-5f mixing in the U₂ π bonds testifies to this. In addition, the calculations identified two strong one-electron bonds mainly of 6d character, and two relatively weak one-electron bonds of 5f character. One may infer a bond order of less than 5 but likely higher than 4 from these findings. The concept of a quintuple bond is certainly intriguing.

D. Dihydrogen

Not only calculations on heavy-element systems benefit from relativistic effects. Consider the celebrated calculations by Kołos and Wolniewicz^{9–11} of the dissociation energy of H₂ which disagreed with the then accepted experimental value of 36 113.6(3) cm^{-1} . The discrepancy was later resolved in favor of quantum theory. Although the relativistic correction was small, -0.5 cm^{-1} , with additional radiative corrections of -0.2 cm^{-1} , it was already somewhat larger than the reported experimental error bars at the time and consequently it had to be included in the theoretical value. See Table I. Jeziorski and co-workers have recently pushed calculations on H₂ and D₂ to new limits (Table I).¹⁴⁶ The H₂ dissociation energy D_0 includes relativistic and QED corrections of $-0.5319(3)$, $-0.1948(2)$, and $-0.0016(8)$ of orders c^{-2} , c^{-3} , and c^{-4} , respectively, and is seen to agree within the error bars with the most recent experimental value.¹⁴⁷ The calculated dissociation energy of D₂ prompted experimentalists to perform a new measurement¹⁴⁸ because of disagreements. The theoretical predictions are seen to be in excellent agreement with the revised experimental value shown in Table I.

E. Electric field gradients, picture change effects

Regarding picture-change effects in 2c calculations, it is noted that in X2C approaches the transformation U is available in matrix form, and therefore molecular property operator matrices for the 2c picture can be constructed in a con-

sistent manner; there should be no picture change errors as a result. Electric properties in 4c calculations may be calculated directly from the 4c density without picture-change errors. Rather common are picture-change errors in quasi-relativistic calculations of electric properties. EFGs have been particularly well studied in this regard, owing to the fact that the differences between 4c and 2c is more pronounced for atomic core and semi-core shells than for valence shells (see discussion of Figure 2 below Eq. (14)). Calculations of EFGs have been reviewed by Schwerdtfeger *et al.*¹⁴⁹ who highlighted the overall importance of relativistic effects on this molecular property. Mastalerz *et al.* have studied picture-change effects on EFGs in detail using higher order DKH transformations⁷⁰ of the EFG operator. For the iodine EFG in the HI molecule, which is a particularly well studied benchmark system, the scalar relativistic DKH result lowered by 11% in total magnitude upon inclusion of picture-change effects. This change amounts to roughly 40% of the relativistic correction and is therefore highly significant. In order to eliminate most of the picture-change errors in order c^{-2} from ZORA calculations of EFGs, van Lenthe *et al.*¹⁵⁰ took the alternative route of reconstructing an approximate 4c electron density in DFT calculations, via applying Eq. (11) with X consistent with the ZORA approximation and subsequent renormalization of the orbital densities (the method was termed ZORA-4). An alternative route obtains the EFG as a derivative of the scaled-ZORA DFT energy expression, leading to the same working ZORA-4 expressions.¹⁵¹ The picture-change corrections between plain ZORA and ZORA-4 reported by van Lenthe *et al.* for the nuclear quadrupole coupling constant of iodine in HI amounted to -5% of the total in calculations with Slater-type basis functions. Spin-orbit effects were on the order of -3% in this case. Likewise, with an alternative implementation of ZORA-4 EFGs using Gaussian basis sets,¹⁵¹ picture-change corrections for the iodine EFG in HI amounted to -5% in scalar relativistic calculations, and -3% in spin-orbit calculations (BP functional). See also Refs. 70 and 152. The calculated iodine EFG of the TI-I diatomic exhibits a particularly large SO effect compared to the overall magnitude of the EFG and its relativistic effects. For example, recent ZORA-4 CAM-B3LYP calculations yielded $V_{33} = 2.06$ (nrel), 2.37 (scalar), and 2.61 (SO) a.u.¹⁵¹ The experimentally derived V_{33} is 2.70 where V_{33} is the largest-magnitude principal component of the negative EFG tensor.

Other electric properties, e.g., static and dynamic polarizabilities, may also be affected strongly by relativity. For examples and references to original research articles see Ref. 21.

F. Hyperfine coupling, J-coupling

An example of a rather dramatic picture-change effect is furnished by the magnetic electron-nucleus hyperfine interaction needed, for instance, to calculate EPR hyperfine coupling and NMR nuclear spin-spin (J -coupling) constants. For a point nucleus, the magnetic vector potential in Coulomb gauge is $\mathbf{A}_N = \boldsymbol{\mu}_N \times \mathbf{U}_N$ where $\mathbf{U}_N = c^{-2} \mathbf{r}_N / r_N^3$. Here, \mathbf{r}_N is the electron-nucleus distance and $\boldsymbol{\mu}_N$ is the nuclear magnetic moment. In Coulomb gauge, $\mathbf{p} \cdot \mathbf{A} = 0$, but $\mathbf{p} \times \mathbf{A}$ which occurs in the nonrelativistic magnetic

perturbation operator (8) (and in form of $\mathbf{p} \times \mathcal{K}\mathbf{A}$ in its ZORA analog, Eq. (23)) is nonzero. Considering that the derivative from \mathbf{p} in space representation acts on everything to its right, one may write $\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p} = \{\mathbf{p} \times \mathbf{A}\}$ where the curly brackets indicate that the derivative only acts on terms enclosed by $\{\dots\}$. Given that μ_N is constant, $\{\mathbf{p} \times \mathbf{A}\} = \{\mu_N(\mathbf{p} \cdot \mathbf{U}_N) - (\mu_N \cdot \mathbf{p})\mathbf{U}_N\}$ in the nonrelativistic case. The derivatives of \mathbf{U}_N give rise to dipolar terms proportional to r_N^{-3} , as well as a delta function $\delta(\mathbf{r}_N)$ which is commonly referred to as the Fermi contact term (FC). In nonrelativistic computations the FC operator samples the density values of s orbitals right at the nuclear positions. The empirical fact that $J(\text{C-H})$ one-bond couplings in NMR are proportional to the s character of the involved carbon¹⁵³ is a consequence of this behavior. In relativistic calculations with point nuclei where the density diverges as $r_N \rightarrow 0$ (see Figure 3), the expectation value of the nonrelativistic FC becomes singular. One may obtain finite matrix elements of the operator in relativistic calculations with finite nuclei, or with an incomplete basis of functions that are finite at the nuclei, but the results would then unphysically depend on the nuclear model or how the basis set is truncated at the nuclei. As an example how the operator is modified in a relativistic framework, the point-nucleus ZORA version of the FC term instead involves $\{\mathbf{p} \times \mathcal{K}\mathbf{A}\} = \{\mu_N(\mathbf{p} \cdot \mathcal{K}\mathbf{U}_N) - (\mu_N \cdot \mathbf{p})\mathcal{K}\mathbf{U}_N\}$ where the presence of \mathcal{K} suppresses the δ term implicit in the expression. For point nuclei, $\mathcal{K} \rightarrow 0$ as $r_N \rightarrow 0$. The matrix elements of the ZORA FC operator remain finite for moderately large Z and the operator matrix elements can be converged in a meaningful way with respect to the basis set size.^{154,155} Instead of sampling a finite electron density at a point nucleus, the quasi-relativistic form of the FC operator samples the density and its slope very close to the nucleus. If one were to use a hyperfine operator that is inconsistent with the approximate or an exact two-component method, such as the nonrelativistic form of the FC term, the results would not be meaningful and become singular in a complete basis. As a note aside, the 4c form of the operator, $\boldsymbol{\alpha} \cdot \mu_N \times \mathbf{U}_N$ does not involve a derivative. However, since the Dirac $\boldsymbol{\alpha}$ matrices couple the upper and lower components of the 4c wavefunction, the derivatives enter the result via the derivatives (from \mathbf{p}) in Eq. (11).

It is interesting to consider the expectation value of the hyperfine coupling operator for the ground state of a hydrogen-like ion case because of the δ function term in the ZORA analog of the FC operator. As long as \mathcal{K} times the density goes to zero at the nucleus, the matrix element stays finite. The ZORA radial density can be calculated from the upper components of the 4c wavefunction upon scaling the coordinate.¹⁵⁶ The 4c upper component radial function for a point nucleus is⁵⁸ $g_{1s}\alpha(Zr)^{\gamma-1}\exp(-Zr)$ with $\gamma = \sqrt{1 - Z^2/c^2}$. That gives a $2c$ density $\rho_{1s}\alpha(Zr')^{2\gamma-2}\exp(-2Zr')$ upon integration over the angular variables, with r' scaled. With $V = -Z/r$, \mathcal{K} goes as $(2c^2/Z)r'$ for very small r' . Thus, $\rho_{1s}\mathcal{K} \propto r'^{2\gamma-1}$ for small r' . This term starts to diverge for $r' \rightarrow 0$ if $\gamma < 0.5$, corresponding to $Z > 118$, in which case the presence of the δ -function term in the FC operator would cause problems. See Ref. 157 for a related discussion of an approximate $2c$ method. The 4c result for a point nucleus would not become singular until $Z > c$, around 137. The antic-

TABLE II. Isotropic ^{199}Hg electron-nucleus hyperfine coupling constants (MHz) for two radicals containing mercury.^a

	HgF	HgAg
nrel. PN	9 173	2 068
DKH2 PN	25 102	4 165
DKH2 FN	21 490	3 456
ZORA PN	21 934	3 450
ZORA FN	19 154	3 109
Expt.	22 163	2 720

^aPN = point nucleus, FN = finite nucleus (Gaussian model), nrel = nonrelativistic, DKH2 data (DFT, B3PW91 functional) from Ref. 158, nrel. and ZORA data (DFT, CAM-B3LYP functional) from Ref. 159. Experimental values as collected in Ref. 193.

ipated breakdown of ZORA hyperfine calculations for point nuclei with $Z > 118$ (basis set permitting) must be attributed to the incomplete (quasi-relativistic) treatment of relativistic effects in conjunction with the strongly singular behavior of the vector potential for a point nucleus. Similar situations be expected for other quasirelativistic Hamiltonians and high Z .

Given the strong inverse dependence of the hyperfine operator(s) on the electron – nucleus distance, one may expect very large relativistic effects on properties that depend on these operators, along with sizable finite-nucleus effects. This is indeed the case. Consider the ^{199}Hg hyperfine coupling constant (HFCC) in the HgF and HgAg radicals listed in Table II, taken from larger data collections reported in Refs. 158 and 159. The relativistic effects actually exceed the magnitude of the nonrelativistic hyperfine couplings for the point-nucleus calculations—for HgF by a large margin. Additionally, there are sizable finite nucleus corrections on the order of 10% to 15%. Hyperfine coupling has been re-investigated recently by Malkin *et al.* using 4c DFT calculations.¹⁶⁰ Finite-nucleus effects for the Cs and Fr atomic HFCCs were reported as -2% and -12% , respectively. For various Hg radicals, the mercury HFCC finite-nucleus corrections were found to be lower than previously obtained from DKH2, on the order of 11% to 15%, and thus more in line with the ZORA data listed in Table II.¹⁵⁹

Regarding the effects from a finite nuclear volume one may conceptually distinguish between two types of effects. First, there is the change in the electronic structure due to the finite nuclear volume¹³³ which is greatly amplified by relativistic effects. A second effect arises from modifications of operators, such as those for hyperfine integrals, due to the finite distribution of the nuclear current density that gives rise to the nuclear magnetic moment. Consideration of finite nuclear current-density distributions affecting the hyperfine structure of heavy elements dates back to early 1950s papers by Bohr and Weisskopf^{161,162} and further back to the early days of modern quantum theory.¹⁶³ See also Ref. 164.

Relativistic and finite-nucleus effects comparable to those for electron-nucleus hyperfine coupling have been reported for NMR J -coupling involving heavy nuclei. For instance, the reduced nuclear spin-spin coupling $K(\text{Hg-C})$ in $\text{Hg}(\text{CN})_2$ was calculated nonrelativistically as $2266 \times 10^{19} \text{ T}^2/\text{J}$, and with scalar ZORA as 4408 (BP functional, point nuclei).¹⁰⁸ Similarly dramatic relativistic effects were reported by Filatov and Cremer with an IORA implementation at the matrix level.¹⁶⁵ The experimental coupling is 5778

in methanol. The difference between the relativistic calculation result and experiment was later shown to be due to solvent effects.¹⁶⁶ Finite nucleus effects on J -coupling constants between Hg and a light atom were shown to be comparable to those of the HFCCs,¹⁵⁵ also reducing the magnitude of the coupling, and of comparable magnitude for Pb (below 10% for Pt). For the Hg–Hg coupling in a crown-ether complex of $[\text{Hg–Hg}]^{2+}$, the finite nucleus effects reached 19%, and went up to 28% for the coupling in the free $[\text{Hg–Hg}]^{2+}$ ion.¹⁵⁵ As far as the magnitude of the Hg–Hg coupling in the crown-ether complex is concerned, a calculation at the hybrid DFT level with finite nuclei¹⁵⁵ determined $K = 771 \times 10^{22} \text{ T}^2/\text{J}$ versus an experimental value of 721. The experimental value translates into the world record for a J -coupling constant: 284 kHz.

Typically, with J -coupling and HFCCs, the dominant effect is from the scalar relativistic increase of the electron density near the nuclei. However, for a large set of J -coupling constants with heavy elements it has been shown that among non-hybrid and hybrid scalar and spin-orbit DFT calculations the best agreement with experiment, on average, is obtained at the SO hybrid DFT level.¹⁶⁷ An example for which SO effects are particularly pronounced is the J -coupling in the Tl–I diatomic. Both the isotropic coupling and the coupling tensor anisotropy are dominated by SO effects.¹⁶⁸

G. NMR shielding, chemical shifts

Many striking examples of relativistic effects on NMR shielding constants and chemical shifts have been documented in the literature. See Refs. 169 and 170 for overviews and pertinent literature. An old example is the heavy-atom effect on chemical shifts of nearby atoms, such as heavy halide atoms bound to carbon in organic compounds. In its purest form it is observed in the H–X series of diatomics, with X = F, Cl, Br, I. For example, Manninen *et al.* calculated the shielding constants with MCSCF wavefunctions and obtained the relativistic corrections via perturbation theory using the Breit-Pauli operator.⁹⁸ Relative to hydrogen fluoride as a reference, the proton shift of HCl was calculated as -2.0 non-relativistically and -2.7 relativistically (expt.: -2.6). For HI, the relativistic effects are very pronounced: -2.7 (nrel) versus -14.6 (rel); the experimental proton shift for HI is -15.3 .¹⁷¹ Such calculations have been repeated numerous times with different relativistic methods and different levels of correlation treatment (including DFT). A collection of calculations performed until 2008 for the proton and halide NMR shifts in HX has been compiled in Ref. 169. It is customary to test new relativistic NMR shielding implementations on the HX series and, occasionally, on rare gas atoms; many of the recent articles reporting new technical advances cited herein provide new data for the HX series. With correlated methods, the results for HI tend to be close to experiment whereas for Hartree-Fock theory the shift is severely overestimated (calculated typically between -19 and -22 ppm). The strong deshielding of the proton in HBr, HI (and HAt) is predominantly caused by SO coupling. For a detailed analysis of such effects see Kaupp *et al.*¹⁷² For NMR parameters of heavy nu-

clei such as Pt, Hg, etc., both scalar and SO relativistic corrections are highly important.²¹

SO effects on chemical shifts of light ligand atoms have also been reported for transition metal complexes with heavy metals. We highlight two recent examples. Hrobarik *et al.* have considered proton chemical shifts in a number of hydride complexes, including the series $[\text{HMCl}_2(\text{PMe}_3)_2]$ with $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$, with the help of 4c DFT calculations.¹⁷³ As an example, for the Ir system, a substantial SO induced proton shielding of about 30 ppm was observed. The correlation between calculated and experimental shifts for the whole range of complexes was substantially improved upon inclusion of SO effects. A strongly increased shielding of ^{29}Si along a Ni, Pd, Pt, triad of novel hypervalent silicon complexes with a direct Si-metal bond has been observed experimentally and, based on ZORA DFT calculations, been attributed to SO coupling.¹⁷⁴ Further, it was shown that SO coupling also has a substantial effect on the ^{29}Si shielding tensor span for the Pt compound.

H. Electron g -factors, zero-field splitting

The deviations of atomic and molecular electronic g -factors from the free-electron value $g_e \approx 2.0023$ may be considered a purely relativistic effect in the sense that such deviations vanish for vanishing SO coupling, and because SO coupling is a relativistic effect. Thus, g -shifts represent directly observable relativistic effects. Usually, g -shifts are small and reported in parts per thousand (ppt). A 4c DFT implementation utilizing non-collinear spin-densities has been reported recently.¹⁷⁵ In a series of test calculations on d^1 metal complexes, it was found that higher-order SO effects in g -shift calculations may be larger than previously thought.¹⁷⁶ An interesting case with a particularly large g -shift is NpF_6 (along with other actinide-hexahalides); the accepted experimental g -factor is -0.6 implying a g -shift on the order of -2600 ppt. The experimentally derived g -factor has been reproduced well by SO CASPT2 calculations¹⁷⁷ and more recently by ZORA DFT calculations.^{178,179}

For additional examples and broader coverage of the literature on relativistic NMR and EPR calculations the reader is referred to some of the available reviews.^{21,169,170,180–182} Another property that plays a role in EPR and other spectroscopic techniques for paramagnetic molecules (e.g., magnetocircular dichroism) is the zero-field splitting. There have been important recent advances regarding the calculation of this property; see Schmitt *et al.*¹⁸³ and references therein.

I. Contact densities

Knecht *et al.* recently performed a theoretical study of Mössbauer isomer shifts of mercury in the series HgF_n with $n = 1, 2, 4$.¹⁸⁴ DFT was compared to CCSD(T) reference data and found to under-perform. Isomer shift calculations have traditionally relied on determining the “contact” density, i.e., the density value at the nucleus of interest. With a point-nucleus, this makes sense in nonrelativistic calculations but not in relativistic calculations where the density diverges (Figure 3). With a finite nucleus, $\rho(0)$, the density at $r = 0$, remains finite and may be used in calculations where contact

densities are needed. Knecht *et al.* considered a Gaussian finite nucleus model in 4c and 2c DKH relativistic calculation, along with a treatment of picture-change effects in the latter case. (Picture-change effects on DKH contact densities were also explicitly investigated in Ref. 185.) A reduction of about 10% of Mössbauer isomer shifts was obtained when using an effective contact density, integrated over the finite nuclear volume, as compared to using $\rho(0)$ values. This effect has been confirmed by scalar relativistic NESC calculations of Mössbauer isomer shifts reported by Filatov *et al.*¹⁸⁶ At the uncorrelated HF theory level, the nonrelativistic calculations of Ref. 184 underestimated the changes in the contact densities when going from the Hg atom to the molecules by factors of 10 or more. In a related study, Mastalerz *et al.* investigated the convergence of relativistic electron densities at the positions of finite nuclei with respect to the size and contraction schemes of Gaussian basis sets.¹⁸⁷ Knecht and Saue recently considered the derivative of the effective contact density with respect to the internuclear distance for a series of heavy diatomic molecules (TlI, PbTe, PtSi), with the aim of modeling the isotopic field shift in the rotational spectra with the help of 4c relativistic calculations.¹⁸⁸ Finite nuclear volume effects were found to be on the order of 10%, with associated relativistic contact density derivatives being roughly an order of magnitude larger than the nonrelativistic results, in agreement with the findings of the aforementioned Mössbauer isomer shift study. Consideration of the picture change of the density operator in related 2c calculations was found to be mandatory.

IV. OUTLOOK

The treatment of relativistic effects in molecular quantum chemical calculations has made tremendous progress. Dealing with electron correlation in such calculations, either by correlated wavefunction methods or by relativistic DFT, remains a work in progress.⁵⁰ The state-of-the-art and remaining challenges in relativistic DFT have been reviewed recently by van Wüllen.¹⁸⁹ It remains to be seen whether the lack of a consistent derivation of a relativistic many-electron Hamiltonian from a more general theory will eventually cause practical problems, or if DCB based theories with QED corrections will suffice. In practical applications the correlation problem presents a major accuracy bottleneck. If a full four-component or X2C relativistic treatment is too expensive in terms of the required computational resources, there are various variationally stable approximate two-component all-electron Hamiltonians as well as relativistic ECPs available that allow for very efficient quasirelativistic calculations. Among the all-electron methods that have found widespread use are ZORA and DKH, in particular DKH2. For many applications, the relativistic treatment by these operators may often be good enough for the desired target accuracy. For example, ZORA (and scaled ZORA) as well as DKH2 tend to furnish sufficiently accurate relativistic effects for and outer core shells in heavy element compounds in order to allow for meaningful calculations of many spectroscopic, structural, and energetic properties at correlated theory levels that are presently in widespread use. For core shell properties of heavy element compounds, plain ZORA affords large errors

and should not be used. The “scaled ZORA” variant offers significant improvements²⁶ at little extra computational cost. Obviously, for very high accuracy calculations the best available treatment of relativistic effects should be used. Errors from an incomplete relativistic treatment may in this case be comparable or larger than the errors from basis set truncation or level of correlation. Finally, it is worthwhile repeating the often stated fact that relativistic effects and electron correlation effects are not additive. With regard to a computational model for a molecule that is not in the gas phase and for calculations at finite temperature, similarly non-additive effects may arise, for instance, from solvent effects or vibrational corrections of calculated spectroscopic parameters.

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