Review Article

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Is relativistic quantum chemistry a good theory of everything?

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Abstract: The literature on relativistic quantum chemistry is briefly reviewed. The meaning of the main physical terms is qualitatively discussed. The ionization potential and electron affinity of a gold atom are discussed as existing examples on high-accuracy calculations. Very accurate calculations exist for 2-electron atoms. The hyperfine structure in the HD and D_2 molecules was used by Pachucki et al., to obtain an improved deuteron quadrupole moment, *Q*. The remaining, so far excluded, physical contributions are briefly listed. A short answer to the title question is: 'Probably yes'. Finally, a comment is made on the possible connection, or lack of one, between parity non-conservation and the handedness of life.

Keywords: Coinage metal chemistry; Dirac equation; nuclear quadrupole moments; PNC; quantum electrodynamics; quantum science and technology.

Introduction

A 'theory of everything' is physicists' slang for a situation where the basic laws in some area are sufficiently well-known for a number of useful applications to be solved. Our point is that the Dirac–Fock–Breit (DFB) Hamiltonian, possibly completed with some estimates for the dominant quantum electrodynamic (QED) corrections, may be close to such a situation. Such methods could be implemented with electron correlation descriptions, running from Density Functional Theory (DFT) to Coupled-Cluster or Hylleraas-style methods.

The relativistic self-consistent field (SCF) equations were formulated in Cartesian coordinates by Bertha Swirles[1] and, in terms of Racah algebra, by Ian Grant[2–4] for individual atoms. The Dirac equation takes care of relativistic effects, important for heavy elements. The Coulomb law is good as it is. The Breit corrections introduce magnetic interelectronic interactions and, in some forms, the retardation effects. The Racah algebra makes the formulation economic and elegant for atoms.

We have earlier listed some meetings in this area[5] and now list the monographs and give a selection of examples from the literature.

Dedicated to the late Ian P. Grant, FRS (15 December 1930 – 1 March 2025).

Article note: A collection of invited papers to celebrate the UN's proclamation of 2025 as the International Year of Quantum Science and Technology.

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Meetings, treatises and reviews

Meetings on relativistic quantum chemistry

A brief list of some comprehensive meetings on relativistic effects in heavy-element (REHE) systems was given at the REHE-13 conference in Assisi in 2022[5] and at the REHE-14 meeting in Amersfoort in 2024.

Treatises on relativistic quantum chemistry

In addition to the proceedings of the mentioned meetings, some treatises are quoted in Table 1.

The author's own principal review articles from 1978 to 2012 include.[34–37]

A word on theory

The Dirac–Coulomb Hamiltonian (in atomic units) is in first quantization

$$H_{\mathrm{DC}} = \sum_{i}^{N_{el}} h_{\mathrm{D}}(i) + \sum_{i<j} (1/r_{ij}). \tag{1}$$

Here, h_{D} is the one-electron Dirac Hamiltonian

Table 1: Some further treatises since 1930. The REHE meetings[5] and REHE symposia on individual topics are not included.

Year	Author	Title
1930	Dirac[6]	The Principles of Quantum Mechanics
1932	Fock[7]	Introduction to QM
1957	Bethe and Salpeter[8]	QM of One- and Two-Electron Atoms
1961	Rose[9]	Relativistic Electron Theory
1964	Bjorken and Drell[10]	Relativistic QM
1973	Moss[11]	Advanced Molecular QM
1974	T.P. Das[12]	Relativistic QM of Electrons
1986	Lindgren and Morrison[13]	Atomic Many-Body Theory
1986	Pyykkö[14]	RTAM I[a]
1989	Johnson et al.[15]	Rel., QED and Weak Interactons in Atoms
1990	Greiner[16]	Relativistic QM. Wave Equations
1992	Thaller[17]	The Dirac Equation
1993	Labzowsky et al.[18]	Rel. Effects in Spectra of Atomic Systems
1993	Pyykkö[19]	RTAM II[a]
1997	Balasubramanian[20,21]	Relativistic Effects in Chemistry. Parts A and B
1998	Strange[22]	Relativistic QM with Applications in Condensed Matter and Atomic Physics
2000	Pyykkö[23]	RTAM III[a]
2002	Schwerdtfeger[24]	Relativistic Electronic Structure Theory. 1. Fundamentals
2003	Pilkuhn[25]	Relativistic QM
2004	Schwerdtfeger[26]	Relativistic Electronic Structure Theory. 2. Applications
2007	Dyall and Fægri[27]	Relativistic Quantum Chemistry
2007	Grant[28]	RQTAM
2007	Johnson[29]	Atomic Structure Theory
2011	Lindgren[30]	Relativistic Many-Body Theory
2015	Reiher and Wolf[31]	Relativistic Quantum Chemistry
2018	Norman et al.[32]	Principles and Practices of Molecular Properties

[a]The three RTAM books cover 10 369 references. The later electronic version,[33] *rtam.chem.helsinki.fi* of January 2025 brings the total number to over 20 435.

Table 2: The IP and the EA of the Au atom (in eV) from Pašteka et al.[38] (Also quoted in ref. 5).

Method	IP		EA	
	Value	Error	Value	Error
DC-HF	7.6892	−1.5364	0.6690	−1.6396
DC-CCSDTQP	9.2701	0.0446	2.3278	0.0192
+Breit	9.2546	0.0290	2.3188	0.0102
+QED	9.2288	0.0032	2.3072	−0.0014
Exp.	9.2256		2.3086	

$$h_{\mathrm{D}}(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2\beta_i + V_{\mathrm{nuc}}(i). \tag{2}$$

Using this Hamiltonian at the Hartree–Fock level will give the DC-HF values in Table 2. The electron correlation, Breit, and QED contributions can then be added. For a digested review of the theory, see the *Introduction* of Lindgren.[30]

The effects that are still missing (and are much smaller), would be the effects of nuclear volume, nuclear electric polarizability, electric and magnetic hyperfine effects, quantum aspects of nuclear dynamics and parity non-conservation (PNC) effects. For the detailed question, on whether chemistry still needs more physics, we refer to the companion article by Saue.[39]

One of the currently active frontlines is QED. Preliminary estimates for alkali metal or coinage-metal atoms[40,41] suggested that QED would give about –1 % of the kinetic relativistic effect. In that sense the DFB Hamiltonian would be '101 % correct'. The largest contribution to the QED is the repulsive self energy (SE), coming from the zero-point oscillations of the vacuum. The next one is the attractive vacuum polarization (VP).

Some readers of Pure and Applied Chemistry might appreciate a simple qualitative description of the QED terms. First, all QM oscillators have their zero-point oscillations. This includes the electromagnetic (EM) oscillations in vacuum. They make the point-like electrons diffuse and less attracted to the nucleus. This is the self-energy, SE, also called the vacuum fluctuation term.

Second, the empty vacuum can be polarized by creating virtual electron-positron pairs. This additional vacuum-polarization (VP) term will strengthen all Coulomb interactions. Higher-order terms also exist. In contrast to the empty vacuum, the physical vacuum is 'full of life'.

Some applications

The IP and the EA of the Au atom

The convergence of the ionization potential (IP) and the electron affinity (EA) of a gold atom are shown in Table 2 (from Pašteka et al.[38]). The level of theory is Dirac–Coulomb coupled cluster with up to pentuple excitations, CCSDTQP. The frequency-dependent Breit correction for electron-electron interaction is made. The handling of the quantum electrodynamical (QED) corrections is also described in ref. [38]. This total combination brings the IP and EA within 3.2 and 1.4 meV, respectively, from their very precise experimental values.

Very precise few-electron examples

An idea of the present situation on QED corrections in two-fermion systems is given by Margócsy and Mátyus.[42] They compare a correlated but non-relativistic starting point and an $1/Z$ approach. For applications of the latter on He-like systems with Z = 5–30, see Yerokhin et al.[43] (Table 3).

Table 3: Atomic transition energies in two-electron atomic systems (in cm^{-1}).

Transition	Z	Exp.		Theor.	
		Value	Ref.	Value	Ref.
$^3S_1$ - $^3P_0$	5	35 393.627(13)	44	35 393.6211(49)	43
	12	95 851.27(92)	45	95 848.43(11)	43
$^3S_1$ - $^3P_2$	5	35 430.084(9)	44	35 430.0876(22)	43
	12	100 255.9(1.9)	45	100 253.451(57)	43

The deuteron quadrupole moment, Q_d

Pachucki et al.[46] used the experimental nuclear quadrupole coupling constants in the $J = 1$ rotational states of HD and D_2 to extract a value (in fm^2) of

$$Q_d = 0.285699\,(15)\,(18) \tag{3}$$

Here the first error estimate comes from the higher-order relativistic and the QED effects. The second error limit characterizes the experiment. Nonadiabatic effects were found to be important.

Nuclear theory by Filin et al.[47] gives

$$Q_d = 0.2854^{+38}_{-17}, \tag{4}$$

in very good agreement with the molecular result. Potential further improvements of the molecular Q_d are foreseen by Pachucki et al.[46]

A comment on handedness of life

Much has been written on the possible influence of parity non-conservation (PNC) on the homochirality of life on earth, as observed in the L-amino acids of proteins and peptides.[48] An obvious alternative possibility, even in the case of complete energetic equivalence of *L* and *R*, is biological selection. 'Sociology and not physics.' Once there is a majority of one alternative, it pays to follow the crowd. Such a homochiral (*xyzt*) bubble could be limited to our present Earth, or even cover larger parts of the Universe. The experimental evidence could come from ancient or extraterrestrial samples, if the chemistry is the same.

Against this background it is interesting that Weil-Ktorza et al.[48] have just reported evidence for functional ambidexterity of an ancient nucleic-acid binding domain.

Conclusions

The handful of numerical examples shown do preliminarily suggest that the physical principles governing the behavior of small atoms and molecules would be under control, and that the answer to the title question could be 'Yes'.

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