CHEMICAL REVIEWS

REVIEW

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The Physics behind Chemistry and the Periodic Table

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1. INTRODUCTION

Theoretical chemistry could be seen as a bridge from the real physics of the physicists to the real chemistry of the experimental chemists. We hence expect that any measurable property of any chemical object could, in principle, be calculated to arbitrary accuracy, if the relevant physical laws are known. Moreover, as put by Sidgwick,[1] "The chemist must resist the temptation to make his own physics; if he does, it will be bad physics—just as the physicist has sometimes been tempted to make his own chemistry, and then it was bad chemistry."

The first step was the Schrödinger equation since the 1920s. Another major step was the inclusion of relativistic effects, using the Dirac equation or approximations to it, basically since the 1970s (for some early reviews, see refs 2−5). These effects are of essential chemical importance and often explain the differences of the sixth period elements (Cs−Rn) from their fifth period counterparts (Rb−Xe). The latest update on relativistic effects on chemical properties is the companion article.[6]

A classical example on relativistic effects in chemistry is the nobility, trivalency,[7] and yellow color of gold.[3,8,9] Another one is the crystal structure of mercury[10] and probably also the low melting point of mercury.[2] No explicit R/NR (relativistic versus nonrelativistic) studies on liquid mercury seem to exist yet. A third new example is the lead−acid battery. It has just been calculated that, of its 2.1 V per cell, over 1.7 V come from relativistic effects.[11] Without relativity, cars would not start. Numerous further examples exist.

Typical ways of including relativity are the use of pseudopotentials or transformed, approximate Dirac Hamiltonians. Both can be calibrated against full-Dirac benchmarks. For some recent summaries on the methodology, we quote Schwerdtfeger,[12,13] Hess,[14] Hirao and Ishikawa,[15] Dyall and Faegri,[16] Grant,[17] Reiher and Wolf,[18] or Barysz and Ishikawa.[19]

The next physical level brings in the quantum electrodynamical (QED) effects. For light-element problems, such as the hydrogen-atom Lamb shift, precise properties of the hydrogen molecules, or the spectra of the lithium atom, all these effects are already clearly seen, because the accuracy of both theory and experiments is very high. Likewise, the QED effects are conspicuous for highly ionized, heavy, few-electron atoms, such as hydrogen-like gold. For neutral or nearly neutral systems, beyond Li or so, only one order-of-magnitude improvement of the computational accuracy, mainly the treatment of electron correlation with adequate basis sets, is estimated to separate the QED effects from being observed in head-on comparisons of theory and experiment. Examples on such cases are the vibrations of the water molecule[20] or the ionization potential of the gold atom.[21−23]

And that may have been "the last train from physics to chemistry" concerning the fundamental interparticle interactions because among the possible further terms, parity nonconservation (PNC)[24,25] splittings are estimated to lie over 10 powers of 10 further down.[26] Like magnetic resonance parameters, the PNC effects can be directly observed. Apart from being a physical challenge, both these effects give new information on molecules, but they are expected to be far too small to influence molecular structures or normal chemical energetics.

2. THE LEVELS OF THEORY

2.1. The Dirac−Coulomb−Breit (DCB) Hamiltonian

We use the atomic units (a.u., $e = m_e = \hbar = 4\pi\varepsilon_0 = 1$). The Year-2008 standard value of the fine structure constant α is 1/137.035 999 679(94).[27] In atomic units, the speed of light $c = 1/\alpha$.[28−30] Please note that in SI units, c is fixed as 299 792 458 m s^{-1}, but in a.u., it has error limits. The DCB Hamiltonian for electrons

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Table 1. The Ionization Potential, IP, and the Electron Affinity, EA, of the Au Atom from the CCSD Calculations[a] of Eliav et al.[36] and Landau et al.[37]

property	nonrel	rel	expt	exp − rel	QED
IP	7.057	9.197	9.22554(2)	0.0285	−0.0255[22]
					−0.0211[23]
EA	1.283	2.295	2.30861(3)	0.014	

[a] Basis functions up to (spdfghik) were included, and 51 electrons were correlated for Au. The last column gives the calculated additional QED contributions. All contributions in eV.

in nuclear potential V_n can be written as

$$H = \sum_i h_i + \sum_{i<j} h_{ij} \tag{1}$$

The one-particle Dirac Hamiltonian

$$h_i = c\alpha\cdot\mathbf{p} + \beta c^2 + V_n, \quad \mathbf{p} = -i\nabla \tag{2}$$

The two-particle Hamiltonian

$$h_{ij} = h_C + h_B, \quad h_C = 1/r_{ij} \tag{3}$$

$$h_B = -\frac{1}{2r_{ij}}[\alpha_i\cdot\alpha_j + (\alpha_i\cdot\mathbf{r}_{ij})(\alpha_j\cdot\mathbf{r}_{ij})/r_{ij}^2] \tag{4}$$

For h_B there are alternative, frequency-dependent forms, see, for example, Lindgren.[31] In the *Coulomb gauge* used, for a magnetic vector potential **A**, one sets $\nabla\cdot\mathbf{A} = 0$. Then the electron−electron interactions can be taken as instantaneous. The first correction, h_B, to the Coulomb interaction h_C in this gauge physically contains both the interactions between the magnetic moments of the two electrons and retardation effects. The latter are by some authors already regarded as a QED effect. In correlated calculations (beyond single-Slater-determinant, self-consistent-field ones), electron-like projection operators, P, should be added:

$$h_{ij}^{\text{eff}} = Ph_{ij}P \tag{5}$$

This is also called the "no-virtual-pair approximation (NVPA)". The next term after this H was found by H. Araki[32] and J. Sucher.[33] It corresponds to the exchange of two virtual photons. See also Lindgren et al.[34] This term is clearly visible in the accurate studies on the hydrogen molecule, see below. In eq 5, the correlation energy arising from h_B exceeds that arising from h_C beyond $Z = 50$ for He-like systems.[35]

An example on the level of accuracy that can be reached for the gold atom at DCB CCSD (coupled cluster singles and doubles) level is given in Table 1.

We notice that the "exp − rel" and "QED" terms have a comparable size but, unfortunately, opposite signs. The ratio of the QED to relativistic energies is here −0.0255/2.14 or −1.2%, a common result for the ns^1 atoms with $Z \geq 50$.[22] In that sense, the DCB-level relativistic effects were "101% right".

Note finally that the relativistic correction to the Au atom IP is 2.14/9.22554 or 23% of the experimental value. For the experimental EA of the gold atom, the relativistic part is 44%. The Dirac-level relativistic effects are both large and well-established.

2.2. The Next Level: Introducing the QED Terms

2.2.1. Qualitative Discussion. For the valence energies of the heavier elements, the QED contributions should become discernible in the near future. Because these effects are still unknown for most chemists, a qualitative description may be helpful. Apart from section 2.3, we shall mainly discuss atomic examples. Estimates for molecules can be obtained by adding the monatomic contributions, as discussed in section 2.2.2. and section 2.2.4.

We start by considering the electromagnetic (EM) oscillations of the vacuum. Real oscillations of the EM field can be externally induced by electronic devices, atomic transitions, etc. They also are thermally excited for $h\nu \leq kT$ by thermal, blackbody radiation. These are real photons.

However, even at $T = 0$, the zero-point oscillations of the EM field are still there. Very qualitatively, they will shake the point-like Dirac electron and give it a "finite size". This leads to the *vacuum fluctuation* or *self-energy* (SE) contribution. For electrons near a nucleus, it is repulsive, because a part of the Coulomb attraction is lost. Parenthetically, if these zero-point oscillations of the EM field are modified by objects ranging from molecules to macroscopic bodies, this leads to *Casimir forces* between them. A good overview is given by Parsegian.[38]

Second, just as an electric field can polarize a noble-gas atom, by virtual quantum mechanical excitations, the "empty vacuum" can be electrically polarized by creating virtual electron−positron pairs. This leads to the *vacuum polarization* (VP) contribution. For electrons near a nucleus, it is attractive.

Until recent times, there was almost no information on the expected magnitude of the SE and VP terms for the valence electrons of the heavier, neutral or nearly neutral atoms. Thus the question is, could they be chemically relevant? The first estimates were produced by Dzuba et al. for the Cs[39] and Fr[40] atoms. They related the *ns* valence electron Lamb shift of an alkali atom to that of a H-like atom with the same Z by using a quantum-defect formula

$$E^{\text{Lamb}} = \frac{\alpha(Z\alpha)^2}{\pi\nu^3}\left(1 - \frac{\mathrm{d}\delta}{\mathrm{d}n}\right)F(Z\alpha) \tag{6}$$

The α^3 is the expected behavior for a Lamb shift. The Z^4 behavior of a one-electron atom is changed to Z^2 for the valence electron of a many-electron atom, see eq 1 of Dzuba et al.[40] Here δ is the so-called "quantum defect". In a many-electron atom, the Rydberg levels are fitted to a $1/(n-\delta)^2$ behavior, instead of the one-electron $1/n^2$ behavior, and $\nu = n - \delta$ is the effective principal quantum number. The expression in the parentheses yields the electron density at the nucleus. It was derived by Fermi and Segrè.[41] The $F(Z\alpha)$ is defined below in eq 7 and already effectively incorporates the relativistic effects on the wave function. This hydrogen-like approach to the electron density at the nucleus is described in Kopfermann[42] and goes back to Fermi and Segrè.[41]

$$E_{n\kappa}^{\text{SE}}(Z\alpha) = \frac{Z^4\alpha^3}{\pi n^3}F_{n\kappa}(Z\alpha) \tag{7}$$

2.2.2. Vacuum Polarization. To lowest order, the VP part can be described by the Uehling potential.[43,44] It is attractive, a local potential, a property of space, and the same for all elements. The analytical expression for a point nucleus is[45]

$$V_n^{\text{eff}}(r) = -\frac{Z}{r}(1 + S(r)) = V_n + V_{\text{Ue}} \tag{8}$$

$$S(r) = \frac{2\alpha}{3\pi}\int_1^\infty \exp(-2r\chi/\alpha)\left(1 + \frac{1}{2\chi^2}\right)\frac{\sqrt{\chi^2-1}}{\chi^2}\,\mathrm{d}\chi \tag{9}$$

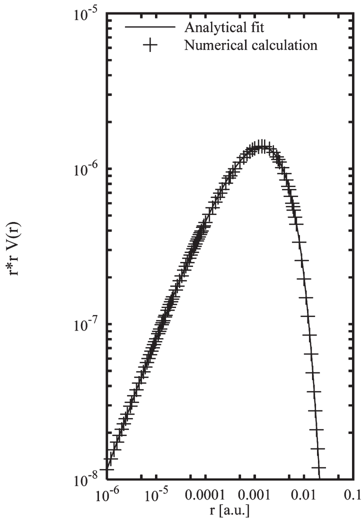

Figure 1. The enhancing Uehling potential, V_{Ue}, eq 8, multiplied by r^2 from the volume element. The points are given by eqs 8 and 9. For the "fit", see ref 21. Reproduced from Pyykkö and Zhao.[46] Copyright 2003 IOP.

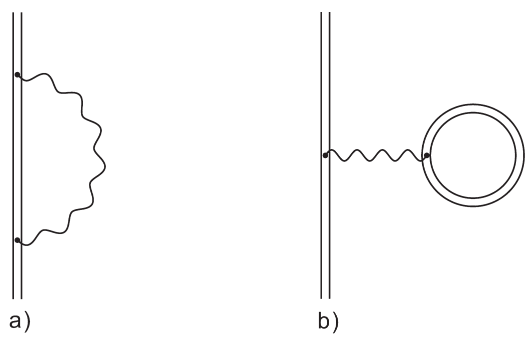

Figure 2. The lowest-order Feynman diagrams for self-energy (a) and vacuum polarization (b). The double solid lines denote the electrons in the atomic potential. The wavy lines are the virtual photons.

The VP effects decay outside ca. 10^{-3} a.u., as seen from Figure 1. Note the factor r^2 from the volume element. The point in the chemical context is that this term is strongly localized to each nuclear neighborhood.

A simple way to include the finite-nucleus changes is to replace the $-Z/r$ in eq 8 by the finite-nucleus V_n.[47] The next-order VP terms are the Wichmann−Kroll[48] and Källen−Sabry[49] ones.

2.2.3. Self-Energy: The Benchmarks. The SE part is larger than the VP and has (for energies) the opposite sign. It can be rigorously treated by first obtaining, for the electrons in question, a complete set of one-particle states at Dirac level, and by then doing the Feynman diagram in Figure 2a. This is known as the *Furry picture*. We then have no "potential" and no "range" for the SE.

The effective atomic potential for that Dirac problem can, in the simplest case, be taken as a suitably parametrized local model potential.[22] If it reproduces the Dirac−Fock (DF) (= relativistic Hartree−Fock) valence eigenvalue, it simulates for the QED purpose a DF model. If it reproduces the experimental IP, it simulates a correlated calculation.

More fundamentally, the effective potential for the QED calculations can be obtained by inverting the radial Dirac−Fock equations.[50] The procedure is as follows: (1) Run first the DF problem to convergence for the system considered. (2) Then "invert" the radial DF equations to get an effective local potential, $V(r)$, for the occupied state A considered. (3) Then solve the Dirac equations for a complete set of excited states, n, in the same potential, with the same basis of radial spline functions. (4) Finally do the Feynman diagram, Figure 2a, in Coulomb gauge using the obtained functions and, for instance, the "multiple-commutator method with partial-wave renormalization"[51]

Table 2. Calculated Electron Affinity of the Noble Gas E118

EA, eV			
DCB (avg)	SE + VP	total	ref
−0.056(10)			52
−0.064(2)	0.0059(5)	−0.058(3)	50

$$\Delta E_{SE}^{A} = \frac{\alpha}{2\pi i}\sum_{n}\left[\frac{1-\vec{\alpha}_1\cdot\vec{\alpha}_2}{\alpha r_{12}} I_{nA}(r_{12})\right]_{AnnA} - \delta m_A \qquad (10)$$

as done earlier for the various model potentials by Labzowsky et al.[22] The method was introduced in ref 51. Here the function

$$I_{nA}(r_{12}) = \int_{-\infty}^{\infty} \frac{d\omega\, \exp(i|\omega|r_{12})}{E_n(1-i0) - E_A - \omega} \qquad (11)$$

refers to the one-electron Feynman diagram, Figure 2a, in the Furry picture for state A and intermediate state n, and $-\delta m_A$ arises from renormalization.

Goidenko et al.[50] found that a 9% reduction of the electron affinity of the noble gas E118[52] was coming from QED effects, see Table 2. Likewise, the earlier results for the valence electrons of group 11 and 12 atoms could be confirmed by the inversion method.[53]

In the lowest-order, low-Z formulation of Bethe[54] (see ref 55), either the self-energy or the entire Lamb shift can be expressed in terms of the electron density at the nucleus.

$$E_1^{\mathrm{Lamb}} = \frac{4\alpha^3 Z}{3}\left[-2\ln(\alpha Z) - \ln X + \frac{19}{30}\right]\langle\delta(\mathbf{r})\rangle \qquad (12)$$

For hydrogen-like atoms, $X = 2K_{n0}/(\alpha Z)^2$ = 11.77, 16.64, 15.93, 15.64, and 15.16 for 1s, 2s, 3s, 4s, and ∞s, respectively, and K_{n0} is the Bethe logarithm (see Labzowsky[56]). For recent reviews on atomic QED calculations, see Beier,[57] Mohr,[58] Eides,[59] Lindgren,[31,34] or Shabaev et al.[60] For a benchmark on self-energy screening in two-electron systems, see Indelicato and Mohr.[61]

The proof of the pudding is in the eating. We show two examples on the size of the various contributions for heavy, highly ionized systems, namely, the energies of hydrogen-like Au in Table 3 and of lithium-like uranium in Table 4. Note the agreement between theory and experiment in both cases. We have chosen H-like Au for the availability of all terms. There are calculations for the remaining SESE terms for both H-like and Li-like heavy ions by Yerokhin et al.[62,63] Concerning the splitting of Li-like U, note the improved nuclear-structure corrections of Kozhedub et al.[64] in Table 4.

An example on a light atomic system is the lithium atom.

We conclude that these calculations may be a patchwork, but they are a patchwork that works. Concerning the convergence, the high-Z approach in Table 3 or Table 4 treats the one-electron relativity to all orders and can treat the virtual-photon exchange

Table 3. Energy Contributions (in eV) for H-like Au[57a]

term	contribution
binding energy, E_T (point nucleus)	**−93459.89**
Corrections	
finite nuclear size	49.13
self-energy (order α)	196.68
VP, Uehling contribution	*−41.99*
VP, Wichmann−Kroll contribution	*1.79*
total vacuum polarization (order α)	−40.20
SESE (2nd-order SE) (a) (b) (c)	uncalculated
VPVP (2nd order VP) (a) (ladder diagrams)	−0.07
VPVP (b) (Källen−Sabry contribution + h.o.)	−0.05
VPVP (c) (Källen−Sabry contribution)	−0.29
SEVP (a) (b) (c)	0.42
S(VP)E	0.05
radiative recoil (estimate)	*0.00*
reduced mass	*0.26*
relativistic recoil	*0.08*
total recoil	0.34
nuclear polarization (*bottleneck for accuracy!*)	−0.02
sum of corrections	205.99
resulting total binding energy	**−93253.90**
total shift (theory)	**205.73**
total shift (experimental)	**202(8)**

[a] The "corrections" are counted from the point-nucleus binding energy. The true electron mass is used everywhere.

Table 4. The 2s−2p$_{1/2}$ Splitting of Li-like U[a]

exptl[65]	280.645(15)
calcd[64] 2008	280.71(10)
calcd[66] 2001	280.47(7)
calcd[67] 2000	280.44(10)
calcd[b]	280.43(7)
inferred two-loop Lamb shift	0.20

[a] From ref 65. [b] J. Sapirstein and K. T. Cheng, as quoted by Beiersdorfer et al.[65]

(the Feynman diagrams) to an arbitrary order. For the low-Z approach in Table 5 or Table 9, the relativistic effects are treated starting from the Pauli Hamiltonian, which itself only must be used as a first-order perturbation. In the calculations quoted, the predominant $(\alpha Z)^4$ terms are, however, included.

2.2.4. Approximate Self-Energy Approaches. How to estimate these effects in molecular calculations? We discuss some existing approximate approaches.

2.2.4.1. The Welton Potential. Welton[71] started from the idea of electromagnetic fluctuations induced by the zero-point oscillations of the vacuum and obtained an effective SE potential, related to $\nabla^2 V_n$. Here V_n is the nuclear potential. Using the fundamentally calculated hydrogen-like SE for calibration, one obtains

$$E_{SE} = \frac{\langle ns|\nabla^2 V_n|ns\rangle_{DF}}{\langle ns|\nabla^2 V_n|ns\rangle_{hyd}} E^{hyd}_{SE,\,ns} \tag{13}$$

Indelicato and Desclaux[72] thus included electronic screening by taking the ratio between Dirac−Fock (DF) and hydrogenic matrix elements. This method has notably been used by Blundell, Desclaux, Indelicato, and coauthors.[72−75] For its nonrelativistic limit, see Dupont-Roc et al.[76]

Table 5. Properties of the ^{7}Li Atom, Calculated by Yan and Drake[68] and by Puchalski and Pachucki[69]

quantity	case	value
IP, cm^{-1}	exptl	43 487.159 40(18)
	calcd (tot)[68]	43 487.172 6(44)
	Lamb (e−n)	−0.305 45(1)
	Lamb (other)	+0.059 478
	calcd (tot)[69]	43 487.159 0(8)
E(2s−2p$_{1/2}$), cm^{-1}	exptl	14 903.648 130(14)
	calcd (tot)[68]	14 903.648 0(30)
	Lamb (e−n)	−0.347 95(1)
	Lamb (other)	+0.043 4721
	calcd (tot)[69]	14 903.648 4(10)
EA, cm^{-1}	exptl	4 984.90(17)
	calcd (tot)[70]	4 984.96(18)

2.2.4.2. Low-Z Approaches. From the Bethe expressions, it is not a long step to treat the relativistic effects at the Breit−Pauli level and, concomitantly, to try to model either the SE part or the entire electron−nuclear Lamb shift, eq 12, by slightly renormalizing its Darwin term, as done by Pyykkö et al.[20]

$$h^{Pauli} = -\frac{\alpha^2}{8}\mathbf{p}^4 - \frac{\alpha^2}{8}\nabla^2 V - \frac{\alpha^2}{4}\sigma\cdot(\nabla V)\times\mathbf{p} \tag{14}$$

with the mass-velocity, Darwin, and spin−orbit contributions, respectively. For a Coulomb potential, $\nabla^2 V = -4Z\pi\delta(\mathbf{r})$. Results were given for the light elements, $Z = 1-54$. Because the Darwin term is strictly local and the V_{SE} is strongly local, it is a reasonable approximation for a molecule to sum them over all nuclei. Assuming that the Bethe-type Coulomb-field Lamb-shift values can be used for many-electron atoms, we obtain at each nucleus the ratio

$$\frac{E_1^{Lamb}}{E_1^{Darwin}} = \frac{8\alpha}{3\pi}\left(-2\ln(\alpha Z) - \ln X + \frac{19}{30}\right) \tag{15}$$

Alternatively, one can use the later QED calculations for one-electron atoms, yielding the ratio of one-electron terms

$$\frac{E_1^{Lamb}}{E_1^{Darwin}} = \frac{2\alpha F(\alpha Z)}{\pi} - \frac{8\alpha}{15\pi} = 4.64564\times10^{-3}F(\alpha Z) - 1.23884\times10^{-3} \tag{16}$$

Here the $F(\alpha Z)$ is related to the SE or the total Lamb shift by an expression of type

$$E_1^{SE} = \alpha^3 Z F(\alpha Z)\langle\delta(\mathbf{r})\rangle \tag{17}$$

The raw data for the function $F(\alpha Z)$ were obtained from the papers of Mohr and co-workers.[58] This resulted in the "eq 6" ratios E_1^{Lamb}/E_1^{Darwin} in Table II of Pyykkö et al.[20] The ratios decrease from 0.04669 for $Z = 1$ to 0.00906 for $Z = 54$, or loosely from 5% to 1%.

An expression, giving the *s*-state Lamb shift as a renormalized Darwin term was already given by Bjorken and Drell in 1964 in the form[77]

$$E_1^{Lamb}/E_1^{Darwin} = (8\alpha/3\pi)\ln(1/Z\alpha) \tag{18}$$

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Table 6. Calculated and Observed Energies (in cm^{-1}) for the Vibrational ($\nu_1\nu_2\nu_3$) States of Water[20]

state	calcd	+Lamb	obsd
(010)	1598.19	−0.09	1594.75
(100)	3657.68	0.18	3657.05
(501)	19776.00	1.01	19781.10

Finally, combining the two-electron Darwin term with the corresponding two-electron Lamb-shift term, we get the ratio

$$\frac{h_2^{\text{Lamb}}}{h_2^{\text{Darwin}}} = -\frac{14\alpha}{3\pi}\ln\alpha = 0.053334 \tag{19}$$

Like the Pauli approximation itself, these equations should be used with nonrelativistic wave functions only.[78]

The derivation above referred to a single atom. For molecules, the strongly local character of the SE permits a summation of these renormalized Darwin terms over nuclei. The first such application were the vibrational levels of water in our own original paper.[20] It was estimated that an improvement of the calculations, at the IC-MRCI/aug-cc-pV6Z level for the valence electrons and lower for the core part, by a further order of magnitude would make the QED contributions to certain vibrational lines of H_2O visible. An example is the (501) "bright state" in Table 6. The experimental accuracy is entirely sufficient for seeing the QED effects.

There are numerous later tests on water, from that of Polyansky et al.[79] to those of Kahn et al.[80] and Császár et al.[81] Both the accuracy of the BO energies, and the nonadiabatic corrections still present obstacles for seeing the QED corrections. Other molecules where this approach has been tested are NH_3,[82] EF_3 (E = B−Ga),[83] H_2S,[84,85] OH, FO, HOF, and F_2O,[86] H_3^+,[87] and CH_2.[88] For more general reviews on high-precision molecular calculations, see Tarczay et al.,[89] Helgaker et al.,[90] or Lodi and Tennyson.[91]

2.2.4.3. The "Ratio Method". Pyykkö et al.[21] noted that the ratio E_{SE}/E_{VP} was fairly constant for given Z, as a function of n. Thus in the *ratio method*, one could multiply the $\langle V_{Ue}\rangle$ by that ratio to get an estimate for the E_{SE}. For heavy elements, the E_{SE} was evaluated from the 2s SE/VP ratio of Johnson and Soff.[92] The total valence-electron Lamb shift became

$$E_L = \langle V_{Ue}\rangle(E_{SE} + E_{VP})/E_{VP} \tag{20}$$

2.2.4.4. Effective Local Potentials.

(a) Another way would be to simulate the SE contribution by local potentials. The first such potential was the modified electron−proton potential for a hydrogen atom, introduced by Pais[93] to account for the hydrogen Lamb shift:

$$V_{\text{Pais}}(r) = -\frac{e^2}{r}[1 - 2e^{-kr}] \tag{21}$$

with k^{-1} on the order of the classical electron radius $r_0 = e^2/(mc^2)$. This reproduced the observed upward 2s shift of about 0.03 cm^{-1}. Note the transition from $-1/r$ at large r to $+1/r$ at small r.

(b) Another potential was proposed by Fricke,[94] who folded the nuclear potential with a Gaussian function $\exp(-\kappa r^2)$

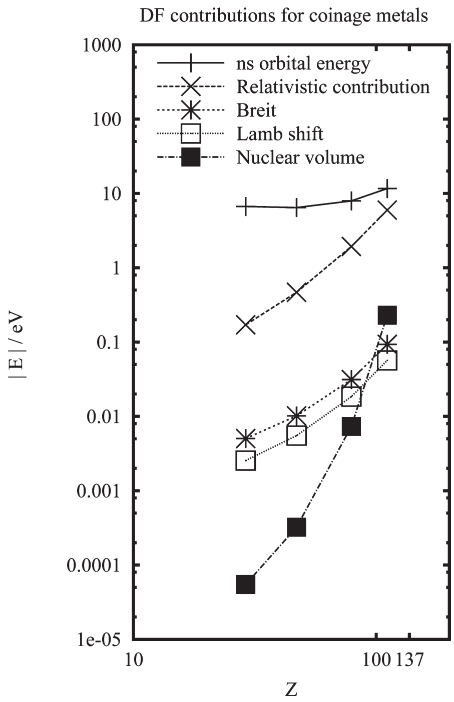

Figure 3. The total Dirac−Koopmans level ionization potentials and their relativistic, Breit, QED, and nuclear-volume contributions[21] for the atoms Cu−Rg. Reproduced from ref 21. Copyright 1998 APS.

with $\kappa = 1/\langle(\delta r)^2\rangle$ and

$$\langle(\delta r)^2\rangle = \frac{2\alpha^3}{\pi}\log(1/(Z\alpha)) \tag{22}$$

(c) If one only wants to reproduce the energy, the "width" of the chosen SE potential is arbitrary and could range from nuclear dimensions to much more diffuse values. Tulub et al.[95,96] introduced a very compact repulsive excess potential of the same shape as that of a homogeneously charged spherical nucleus with radius R_n, for energy levels or for magnetic dipole (M1) hyperfine splittings, respectively. V_0 is a fitting constant.

$$\begin{aligned} V_{\text{QED}} &= V_0\left[1 - \left(\frac{r}{R_n}\right)^2\right], & r < R_n, \\ &= 0, & r > R_n \end{aligned} \tag{23}$$

(d) In the *A-model* of Pyykkö et al.,[21] an extended size was given not to the electron as in the Welton model but to the nucleus. An inflated mass number, A, reproduced the total H-like 2s Lamb shift with

$$A = a\exp(-bZ), \quad a = 2.36 \times 10^5, \quad b = 0.0555 \tag{24}$$

For SE only, $a = 2.09 \times 10^5$ and $b = 0.05001$. The corresponding radius of a homogeneously charged nucleus is $r_A = 2.2677 \times 10^{-5} A^{1/3}$. A comparison of the Dirac-level, Breit, QED, and finite-nuclear-volume effects for the coinage metals Cu, Ag, Au, and Rg is shown in Figure 3.

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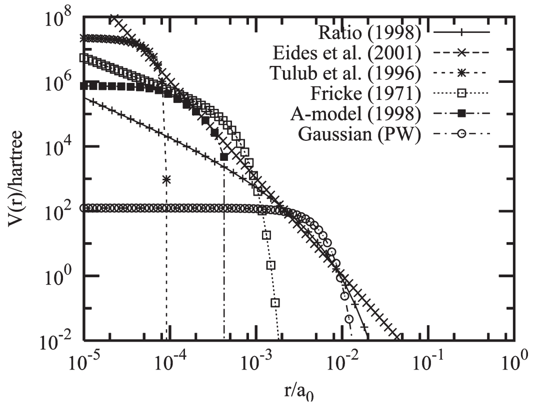

Figure 4. Effective local SE potentials for the *ns* ($n > 1$) electrons of Cs. Reproduced from Pyykkö and Zhao.[46] Copyright IOP.

(e) Eides et al.[59] give a nonrelativistic momentum-space potential whose Fourier transform to *r*-space yields the term

$$V_{SE}(r) = \frac{8\alpha^4 Z(2\pi)^{1/2}}{3r^3} \tag{25}$$

Note that this potential is strongly singular near origin, and it has not been applied to atomic or molecular calculations. As seen from Figure 4, at moderate distances it cuts through many of the alternative potentials.

(f) As mentioned above, the SE energy shifts could be simulated by a potential of any width, from a δ function to atomic dimensions by choosing a suitable precoefficient. If we add other physical properties, also the "width" or shape of the effective SE potential V_{SE} could be semiempirically fitted. Pyykkö and Zhao[46] used the H-like 2s-state Lamb shift and magnetic dipole (M1) hyperfine data of Boucard and Indelicato[97] or Yerokhin et al.[98] to determine the B and β parameters of a two-parameter Gaussian effective potential for all atoms:

$$V_{SE}(r) = B \exp(-\beta r^2) \tag{26}$$

A quadratic polynomial fit, done for both B and β at $29 \leq Z \leq 83$, was still meaningful in the superheavy domain. For a comparison of the different SE potentials for the higher (>1s) s-electrons of Cs, see Figure 4.No molecular applications of this potential have yet been reported.

(g) Flambaum and Ginges[99] derived an effective SE potential from first principles.[100] It has been tested on a number of atoms by Thierfelder and Schwerdtfeger.[23] It contains an SE part with both an electric and magnetic, momentum-dependent potential,

$$V_{QED} = V_{VP} + V_{SE},$$
$$V_{SE}(p) = \left[\frac{g(-p^2)}{2m}\vec{\gamma}\cdot\vec{p} + f(-p^2) - 1\right]\phi(p) \tag{27}$$

whence it cannot be directly compared with the alternative purely electric SE potentials. The numerical agreement with other calculations is good. Here the $\vec{\gamma}$ are Dirac matrices, and g, f, and ϕ are functions depending on the momentum, $\vec{p}$.

(h) Finally we note that hydrogenic estimates, scaled with an effective Z_{eff}, may be useful for inner shells but are not reliable for the valence shells, whose effective field is far from Coulombic. The E_{SE} values, produced by the earlier versions of the Grasp atomic code[101] are of such scaled hydrogenic type.

2.2.5. Summary of Numerical Results for Atoms. Some valence-shell atomic results from various QED approaches are collected for the full Lamb shift to Table 7 and for the SE effects on magnetic-dipole hyperfine interactions in Table 8. Further results on the latter are reported for E119 and $E120^+$ by Dinh et al.[102] Calibration results for M1 hyperfine splittings and g factors of 1s to 3s and 2p states of hydrogen-like ions with $Z = 1-12$ are given by Yerokhin and Jentschura.[103] For further results on the individual SE contributions, see ref 46. The QED corrections to the $p_{1/2}$ states of Li−Cs are discussed by Sapirstein and Cheng.[104] The SE term for E111 (Rg) is reported by Indelicato et al.[105]

For the IP of Be, the estimates by Chung et al.[106] and earlier work, using a Z_{eff}, estimated from the relativistic energy shift, and a Bethe-type $\alpha^3 Z_{eff}^4$ formula, give a 2s Lamb shift of 0.126 meV, rather larger than the later results in Table 7. Estimates for other Be-like systems are also given by them.

Discussing the trends, as seen from Figure 3 for group 11, the valence−*ns*-electron Lamb shifts follow a similar trend as the Dirac-level relativistic effects. It is roughly Z^2, where Z is the full nuclear charge. The sign is a destabilization of the valence *ns* levels. For the outermost, $np_{1/2}$ valence electron of the group 13 elements B−Tl, the sign is negative. For the heaviest member, E113, the sign becomes positive again.

The QED contributions for the discrete 2s−3s transition of a ^{9}Be atom are given to order α^4 by Stanke et al.[107] For the 2s−*ns* transitions of the isoelectronic B^+, see Bubin et al.[108] The contribution to the electron affinity of Li is an increase of 0.007(0) cm^{-1}.[70]

Pachucki and Sapirstein[109] calculated the dipole polarizability of helium. Of the total 1.383 191(2) au, the QED contribution was 0.000 030 au. Łach et al.[110] calculated the full α^3 term and obtained 0.000 030 666(3) au. Their total value is 1.383 760 79(23) au.

Another application area for the QED terms are the inner-shell electronic transitions of neutral or nearly neutral atoms. An example for the superheavy elements E112 to E118 was published by Gaston et al.[116]

We conclude by mentioning the approach by Lindgren et al.[31,117−120] to attack the combined electronic many-body and QED problem from the beginning.

2.3. Accurate Calculations on Diatomics

An extraordinary example of the accuracy of present quantum chemistry are the calculations on H_2 isotopologues,[121] see Table 9. A slight deviation between theory and experiment for D_2 was resolved by a later experiment by Liu et al.[122] The later work includes a measurement[123] and a calculation[124] on HD, see the same table. A finite-nuclear-volume contribution to $D_0(D_2)$ of −0.0002 cm^{-1} is included. For H_2, this correction is estimated to lie below 0.0001 cm^{-1}.[121] Some other species treated are H_2^+ isotopologues,[125−128] $^3He^4He^+$,[129] and He_2.[130]

The background of the H_2 work is well described by Piszczatowski et al.[121] The QED corrections were probably first evaluated by Ladik.[131]

Table 7. The Total Lamb Shift, $E_L = E_{VP} + E_{SE}$ (in meV), for the Valence Shells of Various Groups, G, and Periods (for Their Numbers, See Figure 5) of the Periodic Table for Atomic Systems[a]

		period									
G	A	2	3	4	5	6	7	8	year	ref	eq
1		Li	Na	K	Rb	Cs	Fr	E119			
	DF	0.040	0.28	0.47	1.03	1.92	4.75	17.5[b]	1998	21	eq 20
	DF	0.037	0.27	0.46	1.10	1.85	4.60	17.3	1999	22	eq 10[c]
	DF[d]				1.28	2.23	3.57	10.32	2005	111	eq 13
	DF					2.0	4.5	8.3	2005	99,112	eq 27
	DF[d]	0.033	0.288	0.511	1.298	2.05	4.68	8.96	2010	23	eq 27
	EC					3.5	9.5		1983	39,40	eq 6
	EC	0.051	0.43	0.81	1.99	3.30	7.58		1999	22	eq 10[c]
	EC[g]					2.9	6.5		2002	113	Figure 2
	EC					2.7	5.8	10.6	2005	99	eq 27
2		Be	Mg	Ca	Sr	Ba	Ra	E120			
	DF[d]	0.087	0.419	0.65	1.53[b]	2.35	5.19	9.49	2010	23	eq 27
	EC	0.0722							2007	114	
	EC					4.6[h]	9.5[h]	14.9[h]	2008	112	eq 27
11				Cu	Ag	Au	Rg				
	DF			2.54	5.51	18.42	56.56		1998	21	eq 20
	DF			2.42	5.40	17.5	54.7		1999	22	eq 10[c]
	DF				5.50		56.3		2009	53	eq 10[e]
	DF[d]				6.52		62.6		2009	53	eq 10[e]
	DF[d]			3.05	6.48	21.1	52.9		2010	23	eq 27
	EC			4.61	9.32	25.5			1999	22	eq 10[c]
12				Zn	Cd	Hg	Cn				
	DF				6.17		65.3		2009	53	eq 10[e]
	DF[d]				6.60		69.1		2009	53	eq 10[e]
	DF[d]			3.08	6.43	20.5	52.6		2010	23	eq 27
	DF					26.1[h]			1999	22	eq 10[c]
	EC					32.5[h]			1999	22	eq 10[c]
13		B	Al	Ga	In	Tl	E113				
	DF[d]	−0.23	−0.545	−1.85	−3.07	−5.00	32.4		2010	23	eq 27
	DF					37.1[i]			1999	22	eq 10[c]
	EC					42.0[i]			1999	22	eq 10[c]
18[f]		Ne	Ar	Kr	Xe	Rn	E118				
	DF[d]	−1.012	−1.16	−2.05	−2.47	−3.33	−0.62		2010	23	eq 27

[a] The "approach", A, is either self-consistent field (DF = Dirac−Fock) or includes some estimate of electron correlation (EC). Positive numbers indicate net destabilization. [b] A printing error in original paper is corrected. [c] Full SE calculation in model potentials, simulating DF or IP(exp). [d] Calculated as total-energy differences. [e] Full SE calculation in inverted DF potential. [f] In group 18, period 1, the DF[d] value for He using eq 27 is 0.172 meV.[23] [g] The largest value in various Dirac−Slater potentials chosen. [h] Monocation. [i] Dication.

Calculations for the individual IR lines of hydrogen molecules using NBO-level (non-Born−Oppenheimer) methods are reported for HD by Stanke et al.[134] and for D_2 and T_2 by Bubin et al.[135] HeH^+ was treated in ref 136. Relativistic α^2 corrections were included.

For the finite nuclear mass corrections to electric and magnetic interactions in diatomic molecules, see Pachucki.[137]

2.4. Further Small Terms and Curiosities

2.4.1. The Finite Nuclear Size. The nuclear charge distribution can be taken as a Fermi one[138] with the parameters

$$\rho(r) = \rho_0/[1 + \exp((r - c)(4 \ln 3)/t)] \quad (28)$$

Table 8. SE-Induced Changes of Magnetic M1 Hyperfine Integrals for the Valence Orbitals of ns^1 Metals

	δ, %	
atom	PW (DF)	ref 115
Rb	−0.53	−0.44
Cs	−0.87	−0.75
Fr	−1.77	−1.45
Cu	−0.36	
Ag	−0.78	
Au	−1.58	
Hg^+	−1.44	
Tl^{2+}	−1.38	

Table 9. Dissociation Energies for H_2 and D_2 (in cm^{-1}) from Piszczatowski et al.[121]

order[a]	term	H_2	D_2	HD
α^0	Born–Oppenheimer	36112.5927(1)	36746.1623(1)	
	adiabatic	5.7711(1)	2.7725(1)	
	nonadiabatic	0.4339(2)	0.1563(2)	
	total α^0	36118.7978(2)	36749.0910(2)	
α^2	mass-velocity	4.4273(2)	4.5125(2)	
	one-electron Darwin	−4.9082(2)	−4.9873(2)	
	two-electron Darwin	−0.5932(1)	−0.5993(1)	
	Breit	0.5422(1)	0.5465(1)	
	total α^2	−0.5319(3)	−0.5276(3)	
$\alpha^2 m_e/m_p$	estimate	0.0000(4)	0.0000(2)	
α^3	one-electron Lamb shift	−0.2241(1)	−0.2278(1)	
	two-electron Lamb shift	0.0166(1)	0.0167(1)	
	Araki–Sucher	0.0127(1)	0.0128(1)	
	total α^3	−0.1948(2)	−0.1983(2)	
$\alpha^3 m_e/m_p$	estimate	0.0000(2)	0.0000(1)	
α^4	one-loop term	−0.0016(8)	−0.0016(8)	
total theory		36118.0695(10)	36748.3633(9)[b]	36405.7828(10)[c]
exptl[132]		36118.062(10)	36748.343(10)	
exptl[133]		36118.0696(4)		
exptl[122]			36748.36286(68)	
exptl[123]				36405.78366(36)

[a] The terms are classified by powers of the fine-structure constant, α. [b] Includes −0.0002 cm^{-1} from the finite deuteron size. [c] Pachucki and Komasa.[124]

where ρ_0 is a normalization constant to obtain a charge Z and the surface thickness $t = 2.3$ fm (Fermi) for $Z > 45$. Using

$$A = 0.00733Z^2 + 1.3Z + 63.6 \tag{29}$$

for the atomic mass, the rms nuclear radius c (in fm) is extrapolated in the program from known values of c as a function of $A(Z)$ for large Z.

For recent reviews on the finite nuclear charge distributions and their inclusion in quantum chemistry, see Andrae.[139,140] Ultimately one needs an explicit, quantum-mechanical description of both the nucleus and the electrons. In refs 141 and 142, the authors treated the exchange of virtual photons between a ^{209}Bi nucleus "valence proton" and a single valence electron.

2.4.2. Nuclear Electric Polarizability. Because the nucleus itself has an electric polarizability, α_n, an electron at distance r will enjoy a further attraction

$$V = -\alpha_n/(2r^4) \tag{30}$$

This term is actually thought to limit the accuracy of the calculation on H-like Au in Table 3. A novel application of this polarizability would be a van der Waals-bound dineutron, the ultimate noble-gas molecule.[143]

2.4.3. "Nuclear Relativity". Could the relativistic dynamics of the nuclei become relevant? The question is of principal interest in the NBO calculations (see section 2.3) where the electronic and nuclear motions are handled on equal footing. For a spin-$^1/_2$ nucleus with an anomalous magnetic moment κ,

$$h_{BP} = -\frac{p^4}{8m^3c^2} + \frac{1+2\kappa}{8m^2c^2}\nabla^2 V + \frac{1+2\kappa}{4m^2c^2}\frac{V'}{r}\mathbf{L}\cdot\sigma \tag{31}$$

For a proton, $m = m_p$, the anomalous magnetic moment

$$\kappa = 1.79284734 \tag{32}$$

The expression is adapted from refs 144 and 145 for a spin-zero, infinite-mass potential source.

In their first NBO study, Adamowicz' group[146] neglected this correction. In later work they included it. In practice, this does not matter. Consider as an order-of-magnitude estimate vibrations of frequency ν. Then the critical parameter is $h\nu/(mc^2)$. It therefore seems unlikely that "nuclear relativity" could be seen in many molecular spectra.

For the case of H_2, with the lowest reduced mass of $m = m_p/2 = 918m_e$, we can make the following rough estimate for the relativistic lowering of the various vibrational states, n, using the mass-velocity Hamiltonian h_m, only, and the harmonic estimate $\langle T\rangle = \langle V\rangle = E_n/2$, where the vibrational energy, $E_n = (n + {}^1/_2)h\nu$,

$$\langle h_m\rangle = \langle n| -\frac{p^4}{8m^3c^2}|n\rangle = -\frac{1}{2mc^2}\langle T^2\rangle \approx -\frac{1}{2mc^2}\langle T\rangle^2 = -\frac{1}{8mc^2}\left[\left(n+\frac{1}{2}\right)h\nu\right]^2 \tag{33}$$

The corresponding relativistic change of the transition energy

$$\Delta_r(E_{n+1} - E_n) = -\frac{1}{4mc^2}(n+1)(h\nu)^2 \tag{34}$$

For the lowest, $n = 0$, vibrational transition of H_2, this gives -1.28×10^{-6} cm^{-1}, over 2 orders of magnitude below the estimated inaccuracies of the theoretical[121] and experimental (see Stanke et al.[147]) values of 4161.1661(5) and 4161.1660(3) cm^{-1}, respectively.

Table 10. Relativistic and QED Corrections to 1s-State Hyperfine Splitting of H-like Atoms[a,b]

term	origin	a_{10}	a_{20}	a_{21}	a_{22}	next[d]
Dirac eq	dynamics				$^{3}/_{2}$	$O(\alpha^4 Z^4)$
QED	electron g-factor[c]	$1/(2\pi)$	$-0.328478966/\pi^2$			
QED	vac. pol.			$^{3}/_{4}$		$O(\alpha^3 Z^2)$
QED	self-en.			$\ln 2 - ^{13}/_{4}$		$O(\alpha^3 Z^2)$
total, ppm		1161.4	−1.8	−96.2	79.9	

[a] See Sapirstein[151] and Sunnergren et al.[152] [b] $\Delta E = \Delta E^{NR}[1 + a_{10}(\alpha) + a_{20}(\alpha^2) + a_{21}(\alpha^2 Z) + a_{22}(\alpha^2 Z^2) + ...]$. [c] Electron $g = 2 \times 1.001\,159\,652\,181\,11(74)$. [d] Fine str. const. $\alpha = 1/137.035\,999\,679(94)$.[27]

If a similar harmonic argument were stretched to the dissociation limit, the highest vibrational levels of H_2 would descend by

$$\langle h_m \rangle = \left\langle -\frac{p^4}{8m^3c^2} \right\rangle = -\frac{1}{2mc^2}\langle T^2 \rangle \approx -\frac{1}{8mc^2}(D_0)^2$$
$$= -1.96 \times 10^{-10}\ au = -4.31 \times 10^{-5}\ \mathrm{cm}^{-1} \quad (35)$$

This contribution is less than 2 orders of magnitude beyond the precision of 1×10^{-3} cm^{-1} in Table 9.

It should be added that, as done by Piszczatowski et al.[121] (p 3045), before the small contributions here, one should consider the electron−nucleus Breit interaction and the fact that the accurate "nonadiabatic" wave function depends on the reduced rather than the true mass of the electron. These "nonadiabatic" contributions to the wave function give an $\alpha^2(m_e/m_p)$ contribution to the conventional mass-velocity and Darwin energy.

2.4.4. Magnetic and Hyperfine Effects.

At one-electron Dirac level, one includes these effects via the Hamiltonian

$$h = c\alpha \cdot \mathbf{A} \quad (36)$$

where **A** is the vector potential of the magnetic, external, or nuclear fields.

Beyond Dirac level, the most conspicuous QED effects are those on the g-factor of the electron, see Table 10. The leading Schwinger[148] term, a_{10}, exceeds one part per thousand. The a_{20} term is known as the Karplus−Kroll[149] one. We give in the table the latest available standard value for g. The g calculation by Gabrielse et al.[150] could be inverted to yield α^{-1} = 137.035 999 710(96).

Another example is the magnetic dipole hyperfine splitting of the hydrogen-atom ground state, see Table 10. Here the QED terms a_{10} and a_{21} actually override the leading Dirac term a_{22}.

For the terms arising in the relativistic theory of ESR and NMR variables, see the recent summaries by Aucar et al.,[153] Autschbach,[154−158] Kutzelnigg and Liu,[159,160] or Vaara et al.[161] For all terms at the Breit−Pauli level, see Manninen et al.[162]

Returning to QED effects, for valence ns-state hyperfine interactions near Au, Hg, or Tl, the SE-induced decrease is estimated to be ca. −1.5% per atom,[46] see Table 8. This is comparable with other small effects, such as many examples on solvation.

2.4.5. Retardation at Large Distances.

At large R, retardation will change the R^{-6} dispersion forces to R^{-7} ones. This is of direct importance in a case like He_2, and it is often known as the Casimir effect.[163] For detailed studies, see Przybytek et al.[130] They conclude that 95% of these effects can be included by using the Breit and Araki−Sucher terms.

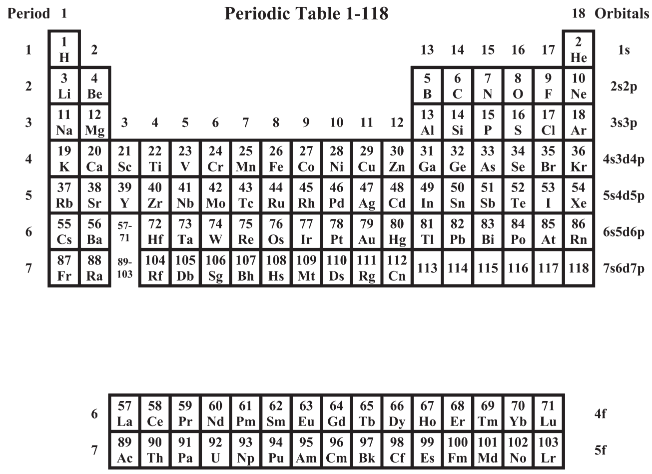

Figure 5. A periodic table for Z = 1−118. Reproduced by permission of the PCCP Owner Societies from Pyykkö.[165] The IUPAC PT[166] coincides with this table, but so far only includes the elements up to roentgenium (E111).

3. THE PERIODIC TABLE

Chemistry is about the chemical elements.[164] These chemical elements can be ordered in a periodic table. The currently experimentally known 118 elements snugly fit to the PT in Figure 5. One case where a chemical property has sizable QED contributions is the electron affinity of the last element, the noble gas E118, see Table 2. Another potentially observable property is the K- and L-shell ionization potentials of E112 to E118.[116]

For the 172 first elements, the PT in Figure 6 was recently proposed on the basis of Dirac−Fock calculations on both atoms and ions.

One reason to discuss the periodic table in the present context are the limits imposed by the spectrum of the Dirac equation in a nuclear (or atomic) field, see Figure 7.

There actually are three special Z values to consider, near 118, 137, and 172. Already Gordon[167] noticed that a unique solution of the Dirac−Coulomb problem (for a point-like nucleus) exists up to $\alpha Z = \sqrt{3}/2$, or $Z \approx 118.7$. Above that, there is another, irregular solution that should be avoided.[168,169] Beyond $\alpha Z = 1$ or $Z \approx 137$, for the electron total angular momentum $j = ^{1}/_{2}$, the dE/dZ would become infinite and the energy E imaginary.[170] Note that the energy in Figure 7 then only reached $-mc^2$. For a finite nucleus, a normalizable solution always exists.[171] With

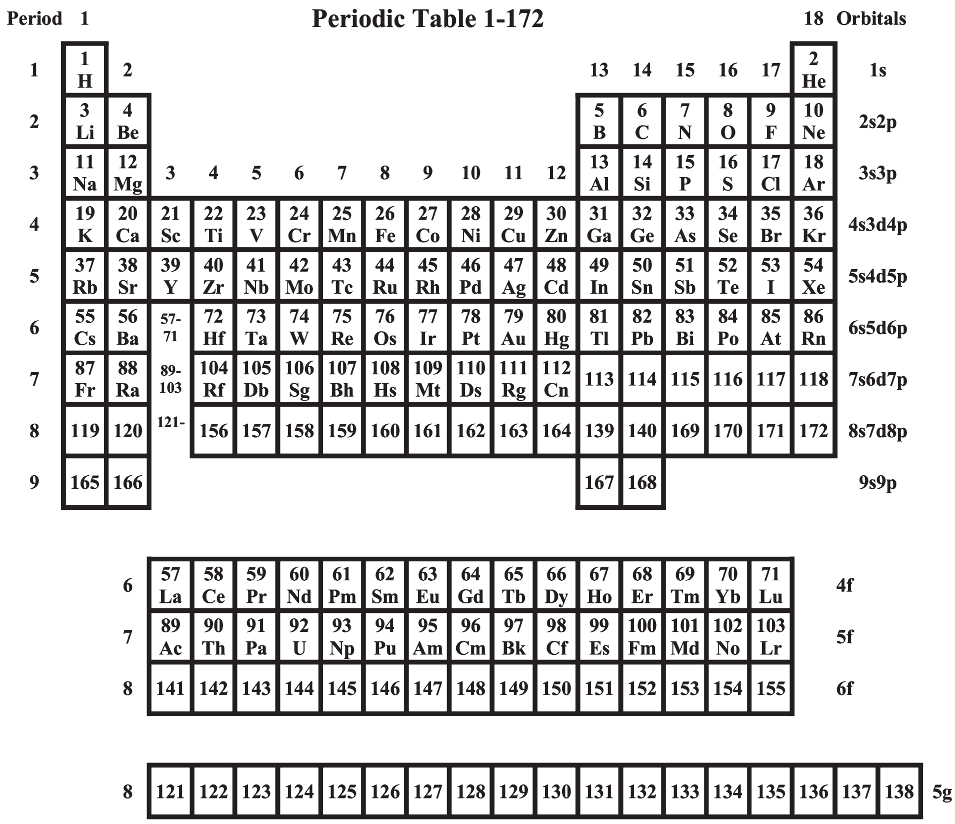

Figure 6. A suggested periodic table for $Z = 1-172$. Reproduced by permission of the PCCP Owner Societies from Pyykkö.[165]

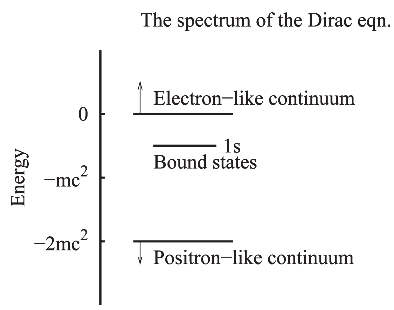

Figure 7. The schematic spectrum of a Dirac electron in an atomic field.

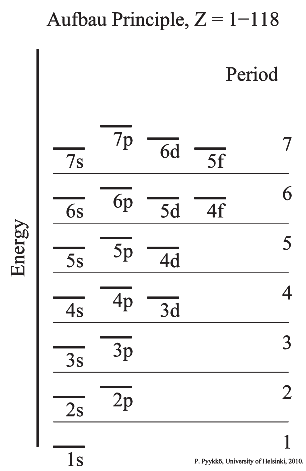

Figure 8. The schematic Aufbau principle for the 118 first elements.

realistic nuclear dimensions, one can go to about $Z = 172$, where the 1s eigenvalue would dive to the lower continuum at $-2mc^2$ (for references, see ref 165). No detailed studies on the actual physical implications for stationary, supercritical systems appear to exist. They may or may not be serious. For the situation in the late 1970s, see Reinhardt and Greiner[172] or Rafelski et al.[173] Anyway, it is reasonable to terminate Figure 6 at $Z = 172$. If the overcritical situation is reached during an atomic collision, a vacancy in the resulting 1s state would fly out as a real positron.

As emphasized by Wang and Schwarz,[174] the periodicity is driven by the noble-gas-like closed-shell structures. The filling order for the 118 first elements is shown in Figure 8.

The next thing to notice is that the first shell of every quantum number l (1s, 2p, 3d, 4f, 5g) is anomalously compact, not having any radial nodes (for details and references, see refs 165 and 175. This makes the second-period elements anomalous, the 2s and 2p shells having similar sizes, despite different energies. The following point is the possibility of partial-screening effects. An example is that selenium is only slightly larger than sulfur, because the $3d^{10}$ shell is filled before it.[176] Another example is the lanthanide contraction, which partially explains the large 6s electron binding energy of Au or Hg.[176,177] The other partial explanation is relativity, which stabilizes the s and p shells and destabilizes the d and f shells, both valence-shell effects roughly increasing as Z^2 down a column and having a local "gold maximum" in group 11[3] along a given period. Indeed, when passing from period 5 to period 6, the main new factor is relativistic effects.[2,178] As an example, the only "normal" coinage metal is silver. Copper is anomalous in having a very compact, nodeless 3d shell. Gold is anomalous due to its large relativistic effects. These mechanisms suffice to $Z = 118$ and beyond.

Beyond $Z = 118$, the next two elements E119 and E120 have $8s^1$ and $8s^2$ electron configurations. Beyond them, the 8p, 7d, 6f, and 5g shells all have a chance to be occupied in a single atom or atomic ion; for earlier literature, see Pyykkö.[165] The placement of the 5g elements in the new periodic table in Figure 6 was fixed by considering ions. For instance, E125(VI) was found to have a $5g^1$ electron configuration, placing E125 in group 7, and the nominal 5g series at $Z = 121-138$. It should, however, be emphasized that considerable overlap may occur between filling the 5g, 8p, 6f, and 7d shells. The broad, general order of atomic levels for the 118 first elements in Figure 8 is followed by

$$8s < 5g \leq 8p_{1/2} < 6f < 7d < 9s < 9p_{1/2} < 8p_{3/2} \qquad (37)$$

as discussed using Dirac–Fock calculations on atoms and ions[165] and already found in the Dirac–Slater atomic work by Fricke et al.[138]

Very few molecular calculations exist yet in this superheavy domain. An early piece of insight was the quasirelativistic multiple-scattering calculation on $[(E125)F_6]$ by Makhyoun[179] finding, indeed, that it was a $5g^1$ system.

Finally we note that low-lying atomic orbitals, which are empty in the atomic single-configuration ground state, can participate in chemical bonding. Examples (in order spdf) are (1) the 8s of E118, (2) the 2p of Li or Be, the 3p of Mg, or the 4p of Zn, (3) the $(n-1)$d of Ca, Sr, and Ba (and Cs), and finally (4) the 5f of Th. In this sense, these four cases could be called *pre-s*, *pre-p*, *pre-d*, and *pre-f* elements, respectively.

4. CONCLUSION

These are all the terms of which news have come to Helsinki. The importance of relativistic (Dirac) effects in heavy-element chemistry is no longer new, but it is useful both to occasionally remind the broad chemical audience about them and to check the soundness of the methods used.

The next physical level, quantum electrodynamics, has a double significance. On one hand, it is about 2 orders of magnitude below the Dirac-level relativistic effects and, being small, thus indirectly verifies the soundness of the latter. On the other hand, quantum chemical methods are becoming increasingly accurate, and it is therefore expected that even these QED terms will soon be needed for fully understanding the chemistry of the heavier elements. For the lightest elements, up to Li or Be, they already have been clearly visible for a long time, because the accuracy is very high. Some extraordinarily accurate work on the H_2 isotopologues has just been reported. Isolated examples of QED effects on the potentially observable properties of the superheavy elements are starting to appear. The relativistic and QED effects together determine many of the chemical trends in and possibly the prescribed upper limit of the periodic table.

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BIOGRAPHY

Photo 2009 by Jussi Aalto.

Pekka Pyykkö was born in Hinnerjoki, Finland, in 1941 and received his education in the nearby city of Turku with a Ph.D. in 1967. His two latest employers were Åbo Akademi University in 1974–1984 and the University of Helsinki in 1984–2009. Since November 2009, he continues research in Helsinki as Professor Emeritus. He now has about 300 papers. He led in 1993–1998 the program "Relativistic Effects in Heavy-Element Chemistry and Physics (REHE)" of the European Science Foundation (ESF) and in 2006–2008 the Finnish Centre of Excellence in Computational Molecular Science (CMS). In addition to his own research, he currently chairs two Academies and one Editorial Board.

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