Estimated valence-level Lamb shifts for group 1 and group 11 metal atoms

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(Received 31 October 1997)

The leading Lamb-shift terms are evaluated for the valence electrons of neutral alkali-metal and coinage metal atoms (groups 1 and 11, respectively). The vacuum polarization (VP) contribution is treated using the Uehling potential and the self-energy (SE) contribution using either a density-based α^3 expression or the E_{SE}/E_{VP} ratios by Johnson and Soff [At. Data Nucl. Data Tables **33**, 405 (1985)]. Both Dirac-Fock and model-potential wave functions are tested. The result for the valence ns electron is a destabilization, rising at moderate Z values (30–80) as Z^2 and more steeply at high Z. The $(n-1)d$ electrons suffer an indirect stabilization. The effects are opposite those of kinetic Dirac relativity and about 1–2% of them. They are roughly half of the valence Breit interaction and rise to about 0.5% of the ionization potential for $Z=111-119$. [S1050-2947(98)51102-X]

PACS number(s): 31.10.+z, 12.20.Ds, 31.30.Jv

I. INTRODUCTION

A large body of literature exists on the quantum electrodynamic (QED) effects in highly charged atoms [1,2]. Apart from lithium [3,4], we are not aware of any estimates of valence-level Lamb shifts for neutral or nearly neutral atoms. If the QED effects are large, they should be evaluated. If they are small, the Dirac-Breit theory is in principle exact to that specific level.

Bethe and Salpeter [5] estimate that the Lamb-shift terms are $\alpha \ln \alpha$ times smaller than the one-electron (fine-structure) relativistic effects, or about -7% of them. For highly charged few-electron atoms the Lamb-shift terms approach the Breit correction to the electron-electron interaction for high nuclear charges, Z [6,7]. We now find similar results, even for the valence electrons of neutral atoms belonging to groups 1 and 11 (alkali metals and coinage metals, respectively).

II. METHOD

The leading Lamb-shift terms are vacuum polarization (VP) and self-energy (SE). Their sum, plus the corresponding higher terms, is the ''Lamb shift.'' We calculate the VP part using the Uehling potential [8] (in atomic units, $e=m_e=\hbar=1$, $c=1/\alpha$),

$$V_n^{\mathrm{eff}}(r)=-\frac{Z}{r}[1+S(r)]=V_n+V_{Ue}, \tag{1}$$

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

The SE part was evaluated in two different ways. For light elements the nonrelativistic density formula [9]

$$E_{SE}=\frac{4Z\alpha^3}{3}\left[\ln\frac{1}{(\alpha Z)^2}-\ln\frac{2K_{n0}}{(\alpha Z)^2}+\frac{5}{6}\right]|\Psi(0)|^2 \tag{3}$$

could be used. The full nuclear Z was then employed. For higher Z we first calculated the VP part as $\langle V_{Ue}\rangle$ and then estimated the SE from the $2s$ E_{SE}/E_{VP} ratio for one-electron

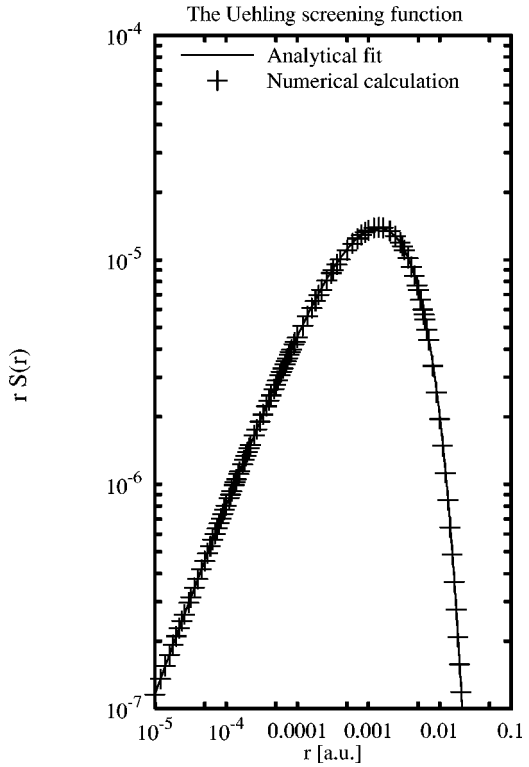

FIG. 1. The Uehling function $rS(r)$. Points from Eq. (2). Analytical fit to Eq. (A1).

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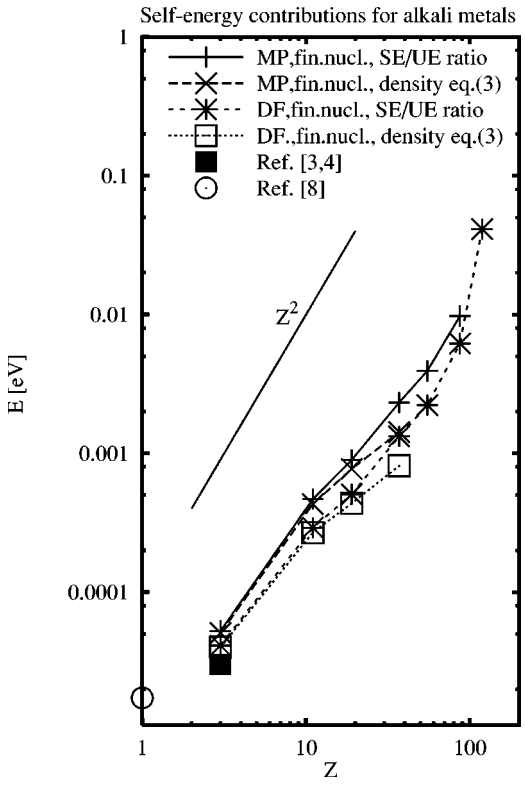

FIG. 2. Self-energy contributions for alkali metals.

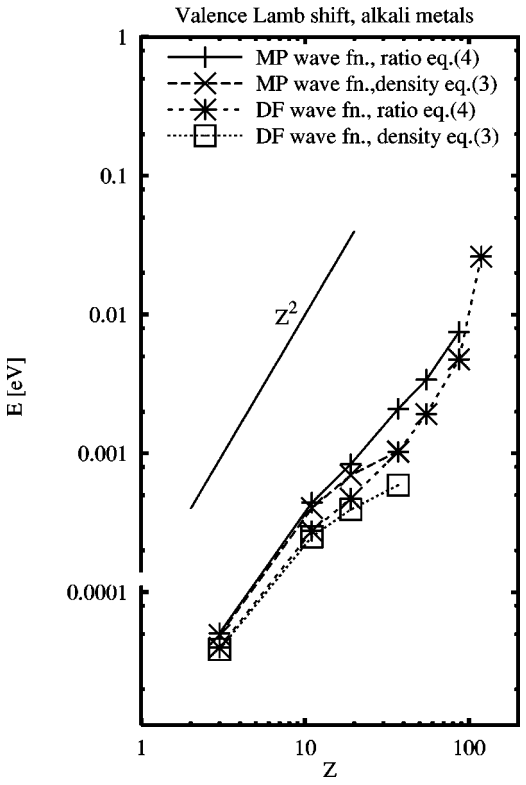

FIG. 3. Total Lamb shifts for alkali metals.

atoms, as calculated by Johnson and Soff [10]. The total valence-electron Lamb shift becomes

$$E_L=\langle V_{\mathrm{Ue}}\rangle(E_{\mathrm{SE}}+E_{\mathrm{VP}})/E_{\mathrm{VP}}. \tag{4}$$

Alternatively the total Lamb shift is obtained to lowest order from the density [5] as

$$E_{\mathrm{L}}=\frac{4Z\alpha^3}{3}\left[\ln\frac{1}{(\alpha Z)^2}-\ln\frac{2K_{n0}}{(\alpha Z)^2}+\frac{19}{30}\right]|\Psi(0)|^2. \tag{5}$$

It should be noted that the VP effect, Eq. (1), stands for an increase of the nuclear Coulomb attraction at small distances r from the nucleus. Weighted by the volume element, the radial distribution of this energy operator $rS(r)$ reaches a maximum at 1.4×10^{-3} a.u., as seen from Fig. 1, for all elements.

The SE part can also be seen as a short-distance effect, as discussed by Welton [11], Fricke [12], or Indelicato and Desclaux [13]. Thus both the VP and SE effects are dominated by the strong Coulomb field near the nucleus that motivates

TABLE I. Calculated ns energies in eV. E_{L} is the total Lamb shift, ϵ the relativistic orbital energy, and IP1 the experimental ionization energy. Δ^{R}, Δ^{B}, and Δ^{V} are the relativistic, Breit [18], and nuclear-volume contributions to ϵ, respectively. The $E_{\mathrm{SE}}/E_{\mathrm{VP}}$ ratio is taken from Johnson and Soff [10]. Other data are Dirac-Fock (DF), except the total Lamb shift where results from the model potential (MP) of Salvat *et al.* [15] are also given, adjusted to $\epsilon=-\mathrm{IP}$.

			E_L						
	E_{VP}	$E_{\mathrm{SE}}/E_{\mathrm{VP}}$	DF	MP	ϵ	$-$IP1[a]	$\Delta^{\mathrm{R}}\epsilon$	$\Delta^{\mathrm{B}}\epsilon$	$\Delta^{\mathrm{V}}\epsilon$
Li	-1.390×10^{-6}	-29.7058	3.991×10^{-5}	5.064×10^{-5}	-5.342	$-5.391\,72$	-4.364×10^{-4}	1.596×10^{-4}	8.0×10^{-8}
Na	-1.550×10^{-5}	-18.7963	2.759×10^{-4}	4.427×10^{-4}	-4.961	$-5.139\,08$	-6.396×10^{-3}	6.888×10^{-4}	2.0×10^{-6}
K	-3.450×10^{-5}	-14.7030	4.729×10^{-4}	8.366×10^{-4}	-4.028	$-4.340\,66$	-1.508×10^{-2}	1.031×10^{-3}	7.0×10^{-6}
Rb	-1.316×10^{-4}	-10.0783	1.027×10^{-3}	2.092×10^{-3}	-3.811	$-4.177\,13$	-5.927×10^{-2}	2.288×10^{-3}	4.48×10^{-5}
Cs	-2.993×10^{-4}	-7.4266	1.923×10^{-3}	3.398×10^{-3}	-3.490	$-3.893\,90$	-1.244×10^{-1}	3.476×10^{-3}	1.86×10^{-4}
Fr	-1.426×10^{-3}	-4.3351	4.754×10^{-3}	7.507×10^{-3}	-3.611	$-4.072\,63$[b]	-4.029×10^{-1}	8.008×10^{-3}	3.20×10^{-3}
119	-1.517×10^{-2}	-2.7796	2.612×10^{-2}		-4.324		-1.330	2.296×10^{-2}	1.29×10^{-1}
Cu	-2.370×10^{-4}	-11.7316	2.543×10^{-3}	4.730×10^{-3}	-6.661	$-7.726\,38$	-1.709×10^{-1}	5.030×10^{-3}	5.48×10^{-5}
Ag	-7.365×10^{-4}	-8.4755	5.506×10^{-3}	8.132×10^{-3}	-6.453	$-7.576\,24$	-4.674×10^{-1}	1.015×10^{-2}	3.23×10^{-4}
Au	-4.614×10^{-3}	-4.9912	1.842×10^{-2}	2.601×10^{-2}	-7.937	$-9.225\,67$	-1.930	3.133×10^{-2}	7.31×10^{-3}
111	-3.181×10^{-2}	-2.7223	5.656×10^{-2}		-11.432		-5.964	9.324×10^{-2}	2.30×10^{-1}

[a]Reference [16].

[b]Reference [17].

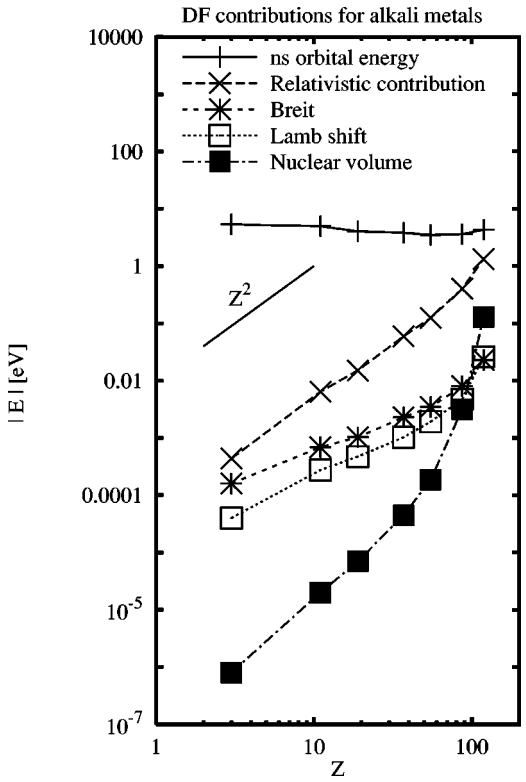

FIG. 4. Comparison of the valence ns Lamb shift with the orbital energy and the relativistic, Breit, and nuclear volume contributions to it for alkali metals at the Dirac-Fock level using Eq. (4).

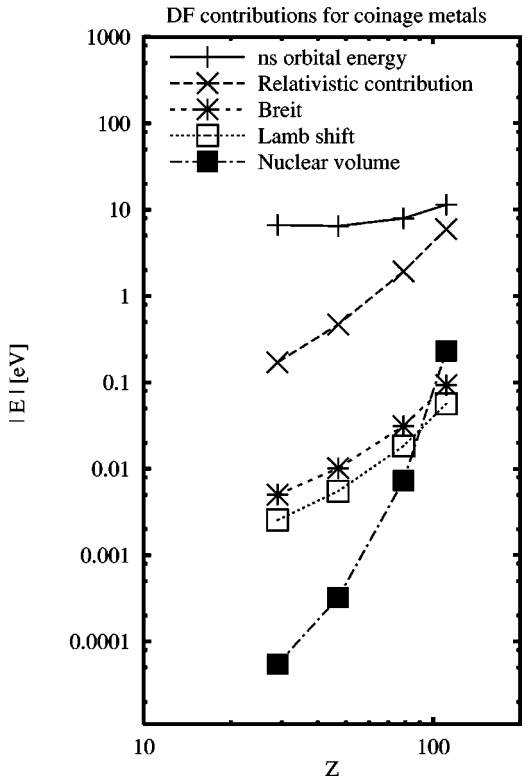

FIG. 5. Comparison of the valence ns Lamb shift with the orbital energy and the relativistic, Breit, and nuclear volume contributions to it for coinage metals at Dirac-Fock level using Eq. (4).

the use of a constant E_{SE}/E_{VP} ratio for all shells. For the $1s$ and $2s$ hydrogenlike states, the ratio is very similar [10]. The effect of the other electrons appears in the amplitude of the s electron near the nucleus.

The valence wave functions were obtained at the Dirac-Fock (DF) level using the program of Desclaux [14]. Independent results were obtained using the local effective potential [model potential (MP)] of Salvat *et al.* [15]. In this case the experimental ionization potential IP_1 was reproduced by adjusting the Slater exchange parameter α_X. A homogeneously charged finite nucleus was assumed. In Eqs. (3) and (5), the electron density at the nuclear surface was used.

III. RESULTS

The self-energies of the alkali metals are shown in Fig. 2. The literature values for hydrogen [9] and lithium [3,4] are included. The total Lamb shifts for the alkali metals are given in Fig. 3.

TABLE II. Ratios of the Lamb shift, E_L, to the relativistic and Breit contributions for the valence ns shells.

	Method	$E_L/\Delta^{\mathrm{R}}\epsilon$	$E_L/\Delta^{\mathrm{B}}\epsilon$
Cs	MP	-1.17×10^{-2}	5.62×10^{-1}
Fr	MP	-9.32×10^{-3}	6.03×10^{-1}
Cu	MP	-1.82×10^{-2}	5.14×10^{-1}
Ag	MP	-1.13×10^{-2}	4.73×10^{-1}
Au	MP	-9.99×10^{-3}	5.95×10^{-1}
	DF	-9.54×10^{-3}	5.88×10^{-1}
111	DF	-9.48×10^{-3}	6.07×10^{-1}

The density expression (3) agrees well with the E_{SE}/E_{VP} ratio results for the SE of Li and Na and starts to deviate from them for K and Rb. For Cs that nonrelativistic SE would even change sign. The two MP curves lie above the two DF ones. The higher MP value should be physically the more correct one.

The Lamb shifts are given in Table I and they are compared to other energy contributions in Figs. 4 and 5. The ratios of the Lamb shift to the relativistic and the valence Breit contributions [18] are shown in Table II. As is well known, the kinetic relativistic effects on the valence shell behave roughly as Z^2. In the middle range ($Z=30-80$) both the valence-shell Breit and the Lamb-shift terms also behave as Z^2. For the highest Z values the increase is faster. The Lamb shift is 1–2% of the kinetic relativistic effect for both alkali and coinage metals. Recall that the latter elements have a ''gold maximum'' of relativistic effects [19]. The Lamb shift is roughly half of the valence-shell Breit contribution, with the same sign.

The nuclear volume effects measure the deviation from a hypothetical point nucleus. They rise faster with Z than the Breit or Lamb ones and would become infinite at $Z=137.036$. They were previously discussed for gold and its compounds by Rösch and co-workers [20]. As seen from Fig. 5, the nuclear volume effect is only slightly below the Breit and Lamb ones for Au.

The kinetic relativistic effects stabilize the ns shells and destabilize the $(n-1)d$ shells of coinage metals. If the potential in Eq. (4) is used self-consistently, we now find that

the d shells are indirectly stabilized roughly as much as the s shells were destabilized.

IV. CONCLUSION

The estimated valence ns-shell Lamb shifts are not entirely negligible. They are of the order of 1–2 % of the kinetic relativistic effects. This means that the existing studies of relativistic effects on chemical properties [19] are 98–99 % correct. The shifts rise to about 0.5% of the orbital energy for $Z=111-119$. Such a percentage should leave the earlier conclusions on the energy levels of elements like Tl and E113 [21] or on the electron affinity of the rare gas E118 [22] qualitatively unchanged.

ACKNOWLEDGMENTS

This work was supported by The Academy of Finland and by the REHE program of ESF. We thank Y. Ishikawa and U. Kaldor for their comments.

APPENDIX: ANALYTICAL FITS

The Uehling function $S(r)$ can be fitted to the two-parameter expression

$$S(r)=\alpha\left[\exp(-d_1r^2)C_1[\ln(\alpha/r)-C_2]+[1-\exp(-d_1r^2)]\left(\frac{\alpha}{C_3}\right)\frac{\exp(-2r/\alpha)}{d_2\left(\frac{r}{\alpha}\right)^{0.5}+\left(\frac{r}{\alpha}\right)^{1.5}}\right]. \quad \text{(A1)}$$

Here the free parameters $d_1=0.678\times10^7$ and $d_2=1.4302$. The three constants

$$C_1=\frac{2}{3\pi},\quad C_2=\frac{5}{6}+C,\quad C_3=4\sqrt{\pi} \quad \text{(A2)}$$

come from the small-r and large-r limiting expressions for $S(r)$ [9] and C is the Euler constant 0.577 21.

The total H-like $2s$ Lamb shift can be reproduced by using the artificially large nuclear mass A of

$$A=a\ \exp(-bZ), \quad \text{(A3)}$$

with $a=2.36\times10^5$ and $b=0.0555$. The nuclear radius $R_n=2.2677\times10^{-5}A^{1/3}$. At the DF level that change of nuclear potential will closely reproduce the results of Eq. (4) for $Z=11-111$.

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