QED radiative corrections and many-body effects in atoms: vacuum polarization and binding energy shifts in alkali metals

J S M Ginges and J C Berengut

School of Physics, University of New South Wales, Sydney NSW 2052, Australia

E-mail: ginges@phys.unsw.edu.au

Received 7 January 2016, revised 11 March 2016
Accepted for publication 22 March 2016
Published 13 April 2016

Abstract

We calculate vacuum polarization corrections to the binding energies in neutral alkali atoms Na through to the superheavy element E119. We employ the relativistic Hartree–Fock method to demonstrate the importance of relaxation of the electronic core and the correlation potential method to study the effects of second and higher orders of perturbation theory. These many-body effects are sizeable for all orbitals, though particularly important for orbitals with angular momentum quantum number $l > 0$. The orders of magnitude enhancement for $d$ waves produces shifts that, for Rb and the heavier elements, are larger than those for $p$ waves and only an order of magnitude smaller than the $s$-wave shifts. The many-body enhancement mechanisms that operate for vacuum polarization apply also to the larger self-energy corrections.

Keywords: vacuum polarization, QED radiative corrections, many-body effects, alkali atoms

1. Introduction

Within the last decade the need has arisen for a method that incorporates quantum electrodynamics (QEDs) radiative corrections into the many-body problem for heavy atoms and ions. For example, account of QED radiative corrections, that is, the vacuum polarization and self-energy corrections, were critical in the interpretation of the measurement [1] of the parity violating amplitude in cesium, which restored an apparent deviation from the standard model of particle physics (see, e.g., [2–9]). There are other areas where full account of QED and many-body effects are required, including in the transition frequencies of many-electron highly charged ions (see, e.g., [10, 11]) and in the spectra and chemical properties of superheavy elements [12]. Ongoing improvements in experimental precision and developments in many-body methods across a range of precision atomic applications necessitate the accurate treatment of combined many-body and QED effects in the generic atomic problem.

The one-loop radiative corrections are made up of the (local) vacuum polarization and the (non-local) self-energy terms The vacuum polarization is dominated by the (lowest order in $\alpha$) Uehling potential, and incorporation of this potential into the many-body problem is relatively straightforward.

The rigorous, highly accurate ab initio procedures for calculating QED self-energy corrections to properties of hydrogen-like and few-electron atoms and ions cannot be applied with the same success to more complex many-body systems (see, for example, the review [13]). There are exact QED calculations performed in frozen atomic potentials (see, e.g., [14, 15]), though here the many-body aspect of the problem may not be readily determined. On the other hand, the QED part of the problem may be simplified and the full many-body treatment employed. Several such ‘radiative potentials’ have been advocated for use in many-body calculations. These include the local potentials [8, 16] and the more sophisticated non-local potential [17], all fitted to self-energy shifts in hydrogenlike ions.

There are a number of recent works where QED radiative corrections have been included into the many-body problem using one or other of these radiative potentials (e.g., [18–21]). However, there has as yet been no in-depth study of the interplay between radiative corrections and many-body effects or of the breakdown of different terms Therefore, it is important to demonstrate the significance of different many-
body effects so that they may be considered appropriately in high-precision calculations.

Derevianko et al. [22] studied the effects of core relaxation on valence s and p level shifts of neutral Cs due to the Uehling potential in the relativistic Hartree–Fock approximation. They demonstrated how important these relaxation effects are, particularly for orbitals with orbital quantum number \( l > 0 \). In this paper we extend the work of Derevianko et al. [22] to include the effects on valence d levels. Inclusion of relaxation corrections leads to several orders of magnitude enhancement of the Uehling correction to the d-level binding energies.

We study also the effect of second- and higher-order many-body perturbation theory on the Uehling correction to valence binding energies through inclusion of the second-order and all-orders correlation potentials. We have found significant corrections to Uehling shifts for all orbitals.

The underlying mechanisms leading to the large many-body effects are studied and calculations are performed for the series of alkali-metal atoms Na through to the superheavy element E119. This work serves as a preliminary study of the more general QED-many-body interplay, where the full radiative corrections (including the larger self-energy) are considered. Since the Uehling potential may be determined to very high precision and is a local operator which may readily be included into atomic many-body codes, the study of the many-body effects is not hindered by any complexity arising from the QED terms themselves. While the form of the self-energy terms is more sophisticated than Uehling, and the radiative shift is generally larger and of opposite sign, the short range of the interaction means that the same many-body enhancement mechanisms apply.

The structure of the paper is the following. In section 2 we present the finite-size form of the Uehling potential used in this work. In section 3, the first-order valence shifts are calculated for frozen atomic cores corresponding to core–Hartree, Kohn–Sham, and Hartree–Fock approximations. The many-body effects of core relaxation and valence–core correlations are studied in sections 4 and 5, respectively. In these sections, details of the many-body enhancement mechanisms are presented and calculations performed for Na through to E119, with more detailed results given for Cs.

### 2. Finite-size Uehling potential

The Uehling potential [23] gives the lowest-order in \( Z \alpha \) vacuum polarization correction to the Coulomb potential \( V_{\text{nuc}}(r) \); \( Z \) is the nuclear charge and \( \alpha \) is the fine-structure constant. For the point-nucleus case, where \( V_{\text{nuc}}(r) = Z/r \), the Uehling potential may be expressed as

\[
V_{\text{Ueh}}^{\text{point}}(r) = \frac{2}{3} \left( \frac{\alpha}{\pi} \right) \left( \frac{Z}{r} \right) \int_1^\infty \frac{dr}{r^2 - 1} \left( \frac{1}{r^2} + \frac{1}{2r^4} \right) e^{-2r/\alpha}.
\]

To obtain the finite-nucleus expression for the Uehling potential, the expression for the point-like nucleus is folded with the nuclear density \( \rho_{\text{nuc}} \)

\[
V_{\text{Ueh}}^{\text{fin}}(r) = \frac{1}{Z} \int d^3 r' V_{\text{Ueh}}^{\text{point}}(r - r') \rho_{\text{nuc}}(r'),
\]

where we use the normalization \( \int \rho_{\text{nuc}}(r) d^3 r = Z \). Taking the nuclear density to be spherically symmetric, and after angular integrations, the well-known finite-nucleus expression for the Uehling potential is obtained

\[
V_{\text{Ueh}}^{\text{fin}}(r) = \frac{2}{3} \frac{\alpha^2}{r} \int_0^r dr' \int_{r'}^\infty dr \sqrt{r^2 - 1} \left( \frac{1}{r^2} + \frac{1}{2r^4} \right) \rho_{\text{nuc}}(r') r' \times (e^{-2r(r')/\alpha} - e^{-2r(r')/\alpha}),
\]

(3)

There are publicly available procedures for performing this integral. For example, the code of Hnizdo [24] or the expansion of Fullerton and Rinker [25]. We will instead consider the case of the step-function density (homogeneous charge distribution) and reduce the double integration, equation (3), to a single integration. The Uehling potential then reduces to the following form, divided into parts valid inside and outside the nucleus

\[
V_{\text{Ueh}}^{\text{step}}(r) = \frac{\alpha Z}{\pi} r \int_0^r dr \sqrt{r^2 - 1} \left( \frac{1}{r^2} + \frac{1}{2r^4} \right) \times \left\{ \begin{array}{ll}
\frac{r}{r_n} & r \leq r_n \\
\frac{r_n}{r_n} e^{-x} (1 + x) \sinh(2r/\alpha) & r > r_n,
\end{array} \right.
\]

(4)

where \( r_n \) is the nuclear radius and \( \alpha = 2r_n/\alpha \). The first term inside the square brackets in the upper line of equation (4) may be simplified by integrating over \( r \) analytically, yielding

\[
\alpha Z \left( \frac{\alpha}{2\pi} \right)^3 \left( \frac{3}{5} \right)\left( \frac{r_n}{r} \right),
\]

where all factors have been included. Equation (4) agrees with that given in [26] in a different form.

Throughout the paper we take \( V_{\text{Ueh}}(r) = V_{\text{Ueh}}^{\text{step}}(r) \) and \( r_n = \sqrt{5/3} r_{\text{rms}} \), where the nuclear root mean square radii \( r_{\text{rms}} \) are taken from [27]. We have found that there is agreement to all digits presented for binding-energy shifts calculated using the step-function density expression for the Uehling potential, equation (4), compared to the full double integral equation (3) with a two-parameter Fermi distribution used for the nuclear density \( \rho_{\text{nuc}}(r) \), provided the same root mean square nuclear radius is used.

In this work the integration of equation (4) is performed using the GNU Scientific Library adaptive integration routine QAGI [28].
The first-order Uehling correction to the binding energies of the valence electron is given by

$$\delta e_i^{(1)} = -\langle \phi_i | V_{\text{eh}} | \phi_i \rangle,$$  \hspace{1cm} (5)

where $\phi_i$ is the valence electron wave function of state $i$.

The zeroth-order valence energies $e_i$ and wave functions $\phi_i$ are found by solving the relativistic equations

$$(e \alpha \cdot p + (\beta - 1) 1/2)^2 - V_{\text{nuc}} - V_\text{d} |\phi_i = e_i |\phi_i,$$  \hspace{1cm} (6)

where $V_{\text{nuc}}$ and $V_\text{d}$ are the nuclear and electronic potentials, $\alpha$ and $\beta$ are Dirac matrices, and $p$ is the momentum operator. We take the nuclear density to correspond to the two-parameter Fermi distribution, with the nuclear thickness (90%–10% fall-off) taken to be 2.3 fm for all atoms and the half-density radius found from the root mean square radii of [27]. For El19, we take $r_{\text{nuc}} = 6.5$ fm, within the range predicted from Hartree–Fock–BFS theory [29].

In this work we consider three different electronic potentials $V_\text{d}$. One is the relativistic Hartree–Fock potential, which we use as our starting point for many-body perturbation theory. We also consider the simpler core-Hartree and Kohn–Sham potentials as points of reference. Labzowsky et al. [14] and Sapirstein and Cheng [15] have calculated the s-wave vacuum polarization (and self-energy) corrections for the alkali metals using several atomic potentials. The core-Hartree and Kohn–Sham potentials were those favored in [15] from the five atomic potentials, based on local density theory, considered in that work.

In the Hartree–Fock approximation, equation (6) is first solved self-consistently for all orbitals of the core, and $V_\text{d}$ represents the direct and exchange Hartree–Fock potentials of the core electrons. The core is then frozen, and the energies and wave functions for the valence electron are found in this potential. (Explicit expressions for the relativistic Hartree–Fock potentials may be found in, e.g., [30].)

In the core-Hartree approximation, the procedure is similar to that for Hartree–Fock, though the exchange potential is altogether excluded. In the Kohn–Sham approximation, a local form for the exchange potential is used,

$$V_{\text{exch}}(r) = \frac{2}{3} \frac{1}{12\pi^2} \rho_\text{tot}(r)^{1/3},$$

where $\rho_\text{tot}(r)$ is the total (core and valence) electronic density, with each electron contributing

$$\rho_\text{tot}(r) = (f_\text{f}(r)^2 + \alpha^2 g(r)^2)/r^2.$$  \hspace{1cm} (The upper and lower radial components of each orbital, $f_\text{f}$ and $g$, respectively, are normalized according to $\int f_\text{f}^2 + \alpha^2 g^2 \, dr = 1$.) The Latter correction [31] is enforced to give the orbitals the correct asymptotic behavior: the total potential $V_\text{tot} = V_{\text{nuc}} + V_\text{d}$ is set to $1/r$ when $V_\text{tot}$ falls below $1/r$. In the Kohn–Sham approximation, equation (6) is solved self-consistently for the core and valence electrons together.

In table 1 we present our results for the first-order Uehling corrections to the s-wave valence binding energies for the alkali atoms Na through to Fr performed in the core-Hartree and Kohn–Sham approximations; we also present our first-order Hartree–Fock results for comparison (a more comprehensive list of Hartree–Fock results is presented later in the table in paper 4). Our core-Hartree and Kohn–Sham results are presented alongside the vacuum polarization calculations of Sapirstein and Cheng [15] performed in the same potentials. As well as taking into account all-orders in $Z$ in the vacuum polarization, the authors of [15] include electronic screening through the use of an effective charge. Both effects act to reduce the size of the Uehling correction. This may explain the deviation between the results.

The core-Hartree and Kohn–Sham results are in fairly good agreement with each other, though reference to the results performed in other atomic potentials [14, 15] shows that there is a sizeable spread in the values, on the order of 10% the size of the shifts. There is also a significant difference between the local atomic potential results and those performed in Hartree–Fock, see table 1. It illustrates how sensitive the vacuum polarization corrections are to the details of atomic structure.

### 4. Core relaxation

The Uehling potential affects the binding energies of the valence electron not only through the direct first-order shift $\delta e_i^{(1)}$, given above, but also indirectly through Uehling corrections to the core electrons. All-orders account of the Uehling correction in the core may be easily determined by adding the Uehling potential to the nuclear potential, $V_{\text{nuc}} + V_{\text{exch}}$, in the relativistic Hartree–Fock equations. Self-consistent solution for the electrons of the core then leads to a new Hartree–Fock potential $V_{\text{HF}}^{\text{exch}}$ which contains a correction due to Uehling $\delta V_{\text{HF}}^{\text{exch}} = V_{\text{exch}}^{\text{exch}} - V_{\text{HF}}$, where $V_{\text{exch}}^{\text{exch}}$ and $V_{\text{HF}}$ are,

| Atom | State | $\epsilon_{\text{CH}}$ | $\delta e_i^{(1)}$ | $\epsilon_{\text{KS}}$ | $\delta e_i^{(1)}_{\text{KS}}$ | $\delta e_i^{(1)}_{\text{HF}}$ |
|------|------|----------------|----------------|----------------|----------------|----------------|
| Na   | 3s1/2| -0.173341     | -7.056[-7]    | -6.888[-7]    | -0.178764     | -6.678[-7]    | -6.573[-7]    | -5.559[-7]    |
| K    | 4s1/2| -0.139522     | -1.497[-6]    | -1.472[-6]    | -0.144032     | -1.431[-6]    | -1.416[-6]    | -1.224[-6]    |
| Rb   | 5s1/2| -0.131786     | -5.274[-6]    | -5.224[-6]    | -0.135854     | -5.202[-6]    | -5.167[-6]    | -4.648[-6]    |
| Cs   | 6s1/2| -0.120057     | -1.131[-5]    | -1.123[-5]    | -0.124015     | -1.133[-5]    | -1.128[-5]    | -1.054[-5]    |
| Fr   | 7s1/2| -0.122884     | -4.556[-5]    | -4.533[-5]    | -0.125432     | -4.642[-5]    | -4.628[-5]    | -4.997[-5]    |
respectively, the self-consistent relativistic Hartree–Fock potentials with and without the Uehling potential included. This correction, $\delta V_{\text{Ueh}}$, is referred to as a relaxation correction. The correction to the energy of the valence electron may then be expressed as

$$\delta \epsilon_i = -\langle \varphi_i | V_{\text{Ueh}} + \delta V_{\text{Ueh}} | \varphi_i \rangle = \delta \epsilon_i^{(1)} + \delta \epsilon_i^{\text{relax}}.$$  \hspace{1cm} (7)

While the source of the relaxation correction is made more transparent from inspection of equation (7), in calculations we instead find the energies $\epsilon_i'$ from the solution of the equation

$$(c \alpha \cdot p + (\beta - 1) c^2 - V_{\text{nuc}} - V_{\text{Ueh}} - V_{\text{HF}}^{\text{Ueh}}) \varphi_i' = \epsilon_i' \varphi_i'.$$  \hspace{1cm} (8)

The correction is then

$$\delta \epsilon_i = \epsilon_i' - \epsilon_i.$$  \hspace{1cm} (9)

It should be noted that the energies from the matrix element equation (7) and from equations (8) and (9) are not equivalent; energies from the solution of the latter equations include higher-order corrections in Uehling to the valence orbitals, while the former equation does not.

In this and the following section we use Cs as our main atom of interest in consideration of the many-body effects core polarization and valence–core correlations, see tables 2 and 3. Our final values for Cs, as well as for the other alkali atoms Na through to E119, are presented in table 4.

In figure 1 we present both the Uehling potential and the Uehling correction to the Hartree–Fock direct potential for Cs. The long range of the relaxation potential makes it possible for all orbitals to receive a relatively sizeable shift from this mechanism. For orbitals with $l > 0$, the relaxation contribution may be orders of magnitude larger than the first-order Uehling contribution, since these orbitals do not penetrate the region close to the nucleus where the Uehling potential acts, making the first-order contribution very small.

The first-order Uehling shifts and the breakdown of the core relaxation contributions for the lowest five valence levels of Cs are presented in table 2. In the second column the first-order results $\delta \epsilon^{(1)}$ are given. In the final two columns, the shifts due to core relaxation are presented, divided into the direct and exchange contributions.

The first-order shift $\delta \epsilon^{(1)}$ is always negative, leading to increased binding, and shifts for the $p$ and $d$ waves are seen to be orders of magnitude smaller than the $s$-wave shift. The direct part of the relaxation potential is of opposite sign to the exchange part. The direct part of the relaxation correction dominates, though the exchange part is also very important, particularly for $5d$. Consideration of core relaxation makes the Uehling shift for $6s$ larger, while it leads to a correction of opposite sign for the other orbitals.

While the magnitude of the relaxation correction for $6s$ is about 10% that of the first-order shift, for the other orbitals the situation is very different. For $6p_{1/2}$, the relaxation correction

| State | $\langle \varphi_i | V_{\text{Ueh}} \varphi_i \rangle$ | Contributions to the relaxation shift, $\delta \epsilon^{\text{relax}} \times 10^6$ |
|-------|---------------------|----------------------------------|
| $6s_{1/2}$ | $-10.538$ | $-0.033 -0.139 -0.164 -0.247 -0.619 -1.211 0.116 0.035 1.573 -2.623$ |
| $6p_{1/2}$ | $-0.194$ | $0.040 0.031 0.027 0.048 0.028 0.430 -0.019 0.012 0.608 -0.185$ |
| $6p_{3/2}$ | $-0.022$ | $0.024 0.026 0.020 0.043 0.315 0.428 0.042 0.004 0.570 -0.096$ |
| $5d_{3/2}$ | $0.000$ | $-0.104 -0.022 0.046 0.081 0.951 0.935 0.153 0.022 0.737 0.390$ |
| $5d_{3/2}$ | $0.000$ | $-0.098 -0.025 0.046 0.083 0.901 0.907 0.068 0.031 0.709 0.298$ |

| State | $\epsilon_{\text{Exp}}$ | Second-order correlation potential $\Sigma^{(2)}$ | All-orders correlation potential $\Sigma^{(\infty)}$ |
|-------|-----------------|------------------|------------------|
| $6s_{1/2}$ | $-0.143098$ | $-0.1470[-5]$ | $-1.470[-5]$ |
| $6p_{1/2}$ | $-0.092166$ | $-0.2856[-7]$ | $-2.856[-7]$ |
| $6p_{3/2}$ | $-0.089642$ | $-3.124[-8]$ | $-3.124[-8]$ |
| $5d_{3/2}$ | $-0.077035$ | $-4.409[-10]$ | $-4.409[-10]$ |
| $5d_{3/2}$ | $-0.076590$ | $-1.015[-10]$ | $-1.015[-10]$ |

| State | $\epsilon_{\text{Exp}}$ | $\delta \epsilon^{(1)}_{\text{Br}}$ | $\delta \epsilon^{(1)}_{\text{Br,fit}}$ | $\delta \epsilon^{(1)}_{\text{Br,fit}}$ |
|-------|-----------------|------------------|------------------|
| $6s_{1/2}$ | $-0.143098$ | $-0.144262$ | $-1.448[-5]$ |
| $6p_{1/2}$ | $-0.092166$ | $-0.092436$ | $-2.895[-7]$ |
| $6p_{3/2}$ | $-0.089642$ | $-0.089848$ | $-3.164[-8]$ |
| $5d_{3/2}$ | $-0.077035$ | $-0.078015$ | $-4.605[-10]$ |
| $5d_{3/2}$ | $-0.076590$ | $-0.077501$ | $-1.018[-10]$ |

$^a$ Data from NIST, [36].

Table 2. Uehling shifts for Cs. First-order valence shifts are shown in column two. Individual contributions of core s orbitals to relaxation shifts are given in columns 3–7, contributions from all core s, all core $p_{1/2}$ and all core $p_{3/2}$ are presented in columns 8–10. In the final two columns the total direct and exchange parts of the core relaxation shifts are given. Units: a.u.

Table 3. First-order Uehling corrections to the binding energies for Cs, $\delta \epsilon^{(1)}_{\text{Br}} = -\langle \varphi_{\text{Br}} | V_{\text{Ueh}} | \varphi_{\text{Br}} \rangle$, where $\varphi_{\text{Br}}$ is a solution of the Brueckner equation ($h_{\text{HF}} + f_0 \Sigma_0 \varphi_{\text{Br}} = \epsilon \varphi_{\text{Br}}$, and the correlation potential $\Sigma$ is the second order $\Sigma^{(2)}$ or all-orders $\Sigma^{(\infty)}$. With no fitting, $f_0 = 1$ and $\epsilon = \epsilon_{\text{Br}}$, while with fitting $\epsilon = \epsilon_{\text{Exp}}$. The numbers in square brackets [ ] denote powers of 10. Units: a.u.
| Atom | State | $\delta E_{HF}$ | $\delta E^{(1)}$ | $\delta E$ | $\delta E_{BL, fit}$ | Other |
|------|-------|-----------------|-----------------|------------|---------------------|-------|
| Na   | 3s\textsubscript{1/2} | -0.182033 | -5.559[-7] | -5.910[-7] | -6.701[-7] | -6.016[-7]\textsuperscript{a} |
|      | 3p\textsubscript{1/2} | -0.109490 | -2.006[-10] | 3.067[-8] | 3.537[-8] |
|      | 3p\textsubscript{3/2} | -0.109417 | -4.101[-11] | 3.077[-8] | 3.548[-8] |
|      | 3d\textsubscript{5/2} | -0.055667 | -6.538[-18] | -1.323[-10] | -1.412[-10] |
|      | 3d\textsubscript{3/2} | -0.055667 | -2.018[-18] | -1.347[-10] | -1.439[-10] |
| K    | 4s\textsubscript{1/2} | -0.147491 | -1.224[-6] | -1.333[-6] | -1.717[-6] | -1.371[-6]\textsuperscript{a} |
|      | 4p\textsubscript{1/2} | -0.095713 | -1.879[-9] | 7.262[-8] | 9.376[-8] |
|      | 4p\textsubscript{3/2} | -0.095498 | -3.547[-10] | 7.396[-8] | 9.524[-8] |
|      | 3d\textsubscript{5/2} | -0.058067 | -1.046[-14] | 1.395[-8] | 4.172[-8] |
|      | 3d\textsubscript{3/2} | -0.058080 | -3.112[-15] | 1.376[-8] | 4.125[-8] |
| Rb   | 5s\textsubscript{1/2} | -0.139291 | -4.648[-6] | -5.114[-6] | -6.767[-6] | -5.288[-6]\textsuperscript{a} |
|      | 5p\textsubscript{1/2} | -0.090816 | -3.234[-8] | 1.776[-7] | 2.365[-7] |
|      | 5p\textsubscript{3/2} | -0.089986 | -4.881[-9] | 2.108[-7] | 2.774[-7] |
|      | 4d\textsubscript{5/2} | -0.059687 | -3.865[-12] | 1.290[-7] | 3.184[-7] |
|      | 4d\textsubscript{3/2} | -0.059745 | -1.048[-12] | 1.218[-7] | 3.001[-7] |
| Cs   | 6s\textsubscript{1/2} | -0.127368 | -1.054[-5] | -1.160[-5] | -1.583[-5] | -1.206[-5]\textsuperscript{a}, -1.054[-5]\textsuperscript{b}, -1.159[-5]\textsuperscript{b} |
|      | 6p\textsubscript{1/2} | -0.085616 | -1.942[-7] | 2.288[-7] | 3.168[-7] | -1.942[-7]\textsuperscript{b}, 2.284[-7]\textsuperscript{b} |
|      | 6p\textsubscript{3/2} | -0.083785 | -2.178[-8] | 4.518[-7] | 6.097[-7] | -2.180[-8]\textsuperscript{b}, 4.513[-7]\textsuperscript{b} |
|      | 5d\textsubscript{5/2} | -0.064420 | -1.938[-10] | 1.127[-6] | 2.516[-6] |
|      | 5d\textsubscript{3/2} | -0.064530 | -4.612[-11] | 1.007[-6] | 2.216[-6] |
| Fr   | 7s\textsubscript{1/2} | -0.131076 | -4.997[-5] | -5.540[-5] | -7.227[-5] | -5.828[-5]\textsuperscript{a} |
|      | 7p\textsubscript{1/2} | -0.085911 | -2.569[-6] | -1.610[-6] | -2.414[-6] |
|      | 7p\textsubscript{3/2} | -0.080443 | -1.356[-7] | 1.834[-6] | 2.408[-6] |
|      | 6d\textsubscript{5/2} | -0.062993 | -3.579[-9] | 3.822[-6] | 8.765[-6] |
|      | 6d\textsubscript{3/2} | -0.063444 | -6.921[-10] | 2.606[-6] | 5.720[-6] |
| E119 | 8s\textsubscript{1/2} | -0.152842 | -3.427[-4] | -4.046[-4] | -4.484[-4] | -4.436[-4]\textsuperscript{a} |
|      | 8p\textsubscript{1/2} | -0.091697 | -3.921[-5] | -4.701[-5] | -7.643[-5] |
|      | 8p\textsubscript{3/2} | -0.075972 | -5.420[-7] | 1.120[-5] | 1.430[-5] |
|      | 7d\textsubscript{5/2} | -0.061414 | -2.517[-8] | 8.715[-6] | 2.594[-5] |
|      | 7d\textsubscript{3/2} | -0.063000 | -4.420[-9] | -1.374[-6] | 9.042[-7] |

\textsuperscript{a}Relativistic HF, perturbative treatment of vacuum polarization, [18].
\textsuperscript{b}First-order relativistic HF results, $\delta E^{(1)}$, [22].
\textsuperscript{c}Relativistic HF with relaxation included, $\delta E$, [22].

IS about twice the size of the first-order shift, which then gives a total shift that is roughly the same size as that of the first-order, though of opposite sign. For 6p\textsubscript{1/2}, the size of the core relaxation correction is of similar magnitude to that for 6p\textsubscript{3/2}, though the smaller first-order correction leads to a much larger (about 20 times) relative correction. For 5d\textsubscript{5/2} and 5d\textsubscript{3/2}, the relative size of the relaxation corrections is enormous; the absolute corrections are about the same size as that for 6s, which makes the Uehling shifts for 5d\textsubscript{5/2} and 5d\textsubscript{3/2} as much as about 10% the size of the 6s shift, and of opposite sign.

While the relative sizes of the relaxation corrections for 4f and 5g orbitals are orders of magnitude larger still, the absolute sizes of the shifts are less than $10^{-4}$ the size of the 5d shifts, so we will not consider the shifts for f and g levels further.

We have looked at the contributions to the direct and exchange relaxation potentials, $\langle \varphi | - \delta V_{dir} | \varphi \rangle$ and $\langle \varphi | - \delta V_{excl} | \varphi \rangle$, for Cs coming from the intervals $r \leq a_B$ and $r > a_B$. As we might expect, from examination of figure 1, most of the direct relaxation shift comes from the interval $r \leq a_B$. While for 6s most of the exchange relaxation shift comes from $r \leq a_B$, for 6p and 5d the largest part of the exchange relaxation shift comes from $r > a_B$.

It is interesting to see how Uehling corrections to individual orbitals of the core propagate in the self-consistent solution of the corrected Hartree–Fock potential and appear finally in the shift in the valence binding energies. In table 2 in the columns 3–10, we consider such shifts. In the columns under 1s through to 5s, we present the shifts to the valence levels that result by switching on the Uehling correction to
these core s orbitals individually. (Note that in this case the potentials for all s orbitals are not the same, resulting in orbitals that are slightly non-orthogonal.)

In columns 8–10 of table 2 we show the contributions to the valence shifts that result by including the Uehling potential for all core s orbitals only, then for all core p_{1/2} orbitals only, and then for all core p_{3/2} orbitals. As we would expect, Uehling corrections to the core s levels give most of the valence shift, though consideration of the contributions from the p orbitals is also important. We have found that the contribution from all d orbitals of the core to the valence shifts for Cs gives a value that is less than 10^{-4} times the size of the shifts from the core s levels; that is, d level valence Uehling shifts are completely determined by the Uehling corrections to the s and p orbitals of the core.

Of the core s levels, the uppermost core s orbital (5s for Cs) gives the largest contribution, many times larger than the contribution from 1s.

This consideration is of significance for the problem of the radiative potentials for use in many-electron atoms, where fitting factors are found by reproducing self-energy shifts in hydrogen-like ions. To good accuracy, radiative potentials need only be fitted to s and p self-energy shifts in hydrogen-like ions; it is not necessary to fit to d shifts. Also, it is more important to optimize the fits for the higher, rather than the lower, core s levels.

Due to the presence of s electrons in the core, one may expect that QED radiative shifts for d-levels for highly charged ions are also determined largely from core relaxation effects. This may change the magnitude and sign of results of exact QED calculations for d-level shifts performed in frozen atomic cores, e.g., in the work [32].

Our results for Na through to E119 are presented in table 4. First-order shifts, shifts with core relaxation included, and shifts with core relaxation and electron–core correlations (to be discussed in the next section) are given. We see similar corrections for the other atoms that we saw for Cs. The effect of relaxation on s levels is significant but moderate, (5 – 20)% . On the other hand, for all other levels, the magnitude and sign of the Uehling shift is determined by the core relaxation correction. There is orders of magnitude enhancement of the d level shifts for all alkali atoms studied. For Cs, the d levels experience a four-orders of magnitude enhancement. There is an almost 8 orders of magnitude enhancement for the 3d_{5/2} level in Na. The relative size of this correction tends to decrease for atoms with higher Z, though remains very sizeable everywhere. For Rb, Cs, and Fr, the Uehling shifts for d levels are larger than those for p levels. For Cs, the d level shifts are only ten times smaller than the s level shifts.

In table 4, the results of Derevianko et al for 6s and 6p levels of Cs are presented in the final column; it is seen that our relativistic Hartree–Fock results agree very well.

The core relaxation corrections to 6s and 6p levels of Cs arising from inclusion of the radiative potential (accounting for vacuum polarization and self-energy) were calculated in [8] and the importance of these effects were noted. The very large corrections for d levels, were seen in our recent work on the spectra of the alkaline earths [20]. The relaxation effect has also been shown to be important in the transition frequencies of several- and many-electron highly charged ions [10, 33], particularly for transitions involving d levels [34], although the relative size of the corrections seen there is significantly smaller than what we have observed in neutral atoms.

5. Correlation corrections

In this section we consider the effect on the valence Uehling shift due to account of higher orders in many-body perturbation theory. The many-body perturbation theory is expanded in the residual Coulomb interaction, 1/|r_i – r_j| + V_d, where V_d is the electronic potential used for the zeroth-order calculations. When calculations are performed in zeroth-order in the relativistic Hartree–Fock approximation, V_{HF} = V_d, as they have been in this work, then the first-order many-body corrections cancel exactly.

The lowest-order many-body corrections then arise in the second order in the Coulomb interaction. The corresponding diagrams, in the Goldstone and Feynman formalisms, may be found, e.g., in [9, 37]. There is a method, developed by Dzuba, Flambaum, and Sushkov [35], for taking into account the higher orders of many-body perturbation theory using the Feynman diagram technique; the Coulomb lines are modified by including an infinite series of core polarization loops and an infinite series of hole-particle interactions in each loop.

A non-local, energy-dependent potential may be determined, with its averaged value corresponding to the correlation correction to the energy. For example, for the second-order case \( \delta \epsilon_{\text{corr}}^{(2)} = \langle \phi | \Sigma_{\text{corr}}^{(2)} (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | \phi \rangle \) while for the all-order case \( \delta \epsilon_{\text{corr}}^{(\infty)} = \langle \phi | \Sigma_{\text{corr}}^{(\infty)} (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | \phi \rangle \). This potential, referred to as the correlation potential, may be added to the Hartree–Fock potential in the relativistic Hartree–Fock approximation.
equations for the valence electrons. This yields Brueckner orbitals \( \varphi_{\text{Br},i} \) and energies \( E_{\text{Br},i} \). Such a procedure also takes into account the higher orders in \( \Sigma \) in the Brueckner orbitals and energies.

In this work we calculate \( \Sigma^{(2)} \) for all atoms considered and we calculate \( \Sigma^{(\infty)} \) for Cs. We calculate \( \Sigma^{(2)} \) using a B-spline basis set \([38]\) obtained by diagonalizing the relativistic Hartree–Fock operator on a set of 40 splines of order \( k = 9 \) within a cavity of radius 40 a.u. The exchange part of \( \Sigma^{(\infty)} \) is also considered in the second-order, with (multipolarity-dependent) factors used to screen the Coulomb interaction. For the direct part of \( \Sigma^{(\infty)} \), the Feynman diagram technique is used for inclusion of the core polarization and hole-particle classes of diagrams; see \([37]\) for further details about the method. The correlation potential method, using all-orders \( \Sigma^{(\infty)} \), has proven to be remarkably successful in high-precision atomic structure calculations for heavy alkali atoms; notably, this method was used to obtain one of the most precise results for parity violation in Cs \([39–41]\).

Inclusion of the correlation potential modifies the orbitals of the valence electrons at large distances, \( r \gtrsim a_B \). These are the distances that also determine the binding energies of the electrons. Placing fitting factors before the correlation potential \( f_\Sigma \), and fitting to the experimental binding energies may be considered a way of taking into account missed effects in the correlation potential. (Experience has shown that, indeed, fitting of the energies leads to improved wave functions at all distances.)

In table 3 we present the Uehling shift for the valence orbitals of Cs with the correlation potential taken into account. We present results both for \( \Sigma^{(2)} \) and \( \Sigma^{(\infty)} \) to see how sensitive the Uehling correction is to the correlation corrections. The values presented in this table do not include the large effects of core relaxation.

It is seen from table 3 that the effect of the correlations is large. They increase the 6s level shift by around 50% and they exceed the relaxation correction for this level. The relative corrections for the other waves is even larger, though for these waves the relaxation effect dominates.

The effect of the correlation potential is to pull the wave functions closer to the nucleus. This leads to larger Uehling shifts for all waves and is more important for the orbitals with \( l > 0 \).

The difference between the results using \( \Sigma^{(2)} \) or \( \Sigma^{(\infty)} \) is significant, affecting the second digit in the results. However, the fitted results shown in columns five and eight of table 3, agree very well, to about 2% for 6s and significantly better for the other waves. That is, as long as the correlation potential is fitted to reproduce the experimental energies, the correlation corrections to the Uehling shifts are insensitive to the details of \( \Sigma \).

Therefore, we have performed calculations for Na through to E119 with the second-order correlation potential \( \Sigma^{(2)} \) fitted to reproduce experimental energies (for E119, we use fitting factors from Fr). These results, which also include the important core-relaxation effects, are presented in the sixth column of table 4.

In the final column of table 4 we present, along with the results of \([22]\), the vacuum polarization calculations performed by Thierfelder and Schwerdtfeger \([18]\) in the relativistic Hartree–Fock approach. Their results are in reasonable agreement with our relaxed core results \( b_r \). We are not aware of other many-body vacuum polarization results for the alkali atoms.

It is worth emphasizing the effect of the correlation potential on the valence electron wave functions. The wave functions are modified by the correlation potential in the region \( r \gtrsim a_B \); see figure 2, where we illustrate the relativistic Hartree–Fock and Brueckner upper radial component for the 6s orbital of Cs. For \( r < a_B \), the Brueckner wave functions are proportional to the Hartree–Fock wave functions, \( \varphi_{\text{Br}}(r < a_B) = c \varphi(r < a_B) \). The effect that the correlation corrections have in this region is simply in the normalization of the wave functions. Obviously, since the Uehling potential acts at a distance close to the nuclear radius, \( \langle \varphi_{\text{Br}} | V_{\text{Ueh}} | \varphi_{\text{Br}} \rangle = c^2 \langle \varphi | V_{\text{Ueh}} | \varphi \rangle \). If the range of the correction to the Hartree–Fock potential \( \delta V_{\text{HF}} \) were within \( a_B \), then \( \langle \varphi_{\text{Br}} | V_{\text{Ueh}} + \delta V_{\text{HF}} | \varphi_{\text{Br}} \rangle = c^2 \langle \varphi | V_{\text{Ueh}} + \delta V_{\text{HF}} | \varphi \rangle \) also, i.e., \( \delta \varepsilon_{\text{Br}} = c^2 \delta \varepsilon = (\delta \varepsilon^{(1)}_{\text{Br}}/\delta \varepsilon^{(1)}) \delta \varepsilon \). We do notice some deviation from this relation, which is a result of the long range of the relaxation correction to the Hartree–Fock potential; this range indeed extends beyond \( r = a_B \), as we saw in the previous section. Overall, though, the relation above holds fairly well.

From consideration of the level of agreement between the fitted Brueckner results of Cs from table 3, we estimate the uncertainty of our final results for the alkali atoms Na to E119 (column six of table 4) to be a few percent.

While the aim of this work is to study the effect of many-body corrections on the QED radiative shifts, applied to the Uehling potential specifically, we note that there are other contributions to the vacuum polarization shift at the one-loop level that we have not included, for instance the higher-order in \( Z \alpha \) corrections and remaining electron screening effects corresponding to a vacuum polarization loop in the photon exchange between electrons. A more precise study would
include these contributions, though we expect them to contribute at a level that is smaller than the estimated uncertainty in this work.

6. Conclusion

We have studied the mechanisms of core relaxation and valence–core correlations on the Uehling shift for the valence levels of the alkali atoms Na to E19. We observe sizeable corrections to the s-level shifts, while for the other orbitals $l > 0$ the relative size of the corrections is larger. For the $p_{1/2}$ orbitals we have seen for several atoms that the relaxation and first-order Uehling shifts are roughly the same size and of opposite sign. For $p_{3/2}$ and for the $d$ levels, the effect of core relaxation is enormous, with corrections being orders of magnitude larger than the first-order result and usually of opposite sign. Account of the valence–core correlations is also important for all waves. For Rh, Cs, and Fr, the d-level shifts become comparable to the size of the s-level shifts (one order of magnitude smaller).

The atomic theory uncertainty for calculations of transition frequencies in heavy neutral alkali atoms is at the level of 0.1% [37], limited by the incomplete treatment of electron–electron correlations. This is roughly the same level where the radiative corrections enter. (The full radiative shift is comprised of the vacuum polarization and self-energy shifts, with the self-energy shift typically an order of magnitude larger than the vacuum polarization shift and of opposite sign.) If the remaining uncertainty in the electronic theory can be controlled, the huge many-body corrections for the radiative shifts for d levels could make high-precision studies of transition frequencies involving these levels a particularly sensitive test of combined QED and many-body effects.

The results of this work are relevant for studies of radiative potentials—potentials that mimic self-energy QED radiative corrections—for use in heavy atoms and ions. The many-body enhancement mechanisms that operate for the Uehling potential apply also to the self-energy due to the short range of the interaction.

Acknowledgments

We are grateful to A Yelkhovsky for useful discussions. The all-order correlation potential $\Sigma^{(\infty)}$ was calculated using the Dzuba–Flambaum–Sushkov codes maintained by V Dzuba. This work was supported in part by the Australian Research Council, grant DE120100399.

References

[1] Wood C S, Bennett S C, Cho D, Masterson B P, Roberts J L, Tanner C E and Wieman C E 1997 Science 275 1759
[2] Sushkov O P 2001 Phys. Rev. A 63 042504
[3] Johnson W R, Bednyakov I and Soff G 2001 Phys. Rev. Lett. 87 233001
[4] Yu Kuchiev M and Flambaum V V 2002 Phys. Rev. Lett. 89 283002
[5] Milstein A I, Sushkov O P and Terekhov I S 2002 Phys. Rev. Lett. 89 283003
[6] Sapirstein J, Pachucki K, Vetia A and Cheng K T 2003 Phys. Rev. A 67 052110
[7] Shabaev V M, Pachucki K, Tupsitsyn I I and Yerokhin V A 2005 Phys. Rev. Lett. 94 213002
[8] Flambaum V V and Ginges J S M 2005 Phys. Rev. A 72 052115
[9] Ginges J S M and Flambaum V V 2004 Phys. Rep. 397 63
[10] Blundell S A 1993 Phys. Rev. A 47 1790
[11] Chen M H, Cheng K T, Johnson W R and Sapirstein J 2006 Phys. Rev. A 74 042510
[12] Schwendt-pfeger P, Pašeta L F, Punnett A and Bowman P O 2015 Nucl. Phys. A 944 551–77
[13] Mohr P J, Plumien G and Soft G 1998 Phys. Rep. 293 227
[14] Labzowsky L, Goidenko I, Tokman M and Pyykkö P 1999 Phys. Rev. A 59 2707
[15] Sapirstein J and Cheng K T 2002 Phys. Rev. A 66 042501
[16] Pyykkö P and Zhao L-B 2003 J. Phys. B: At. Mol. Opt. Phys. 36 1469
[17] Shabaev V M, Tupsitsyn I I and Yerokhin V A 2013 Phys. Rev. A 88 012513
[18] Thirfielder C and Schwendt-pfeger P 2010 Phys. Rev. A 82 062503
[19] Roberts B M, Dzuba V A and Flambaum V V 2013 Phys. Rev. A 87 050402
[20] Ginges J S M and Dzuba V A 2015 Phys. Rev. A 91 042505
[21] Sato T K et al 2015 Nature 520 209
[22] Derevianko A, Ravaine B and Johnson W R 2004 Phys. Rev. A 69 050452
[23] Uehling E A 1935 Phys. Rev. 48 55
[24] Hnizdo V 1994 Comput. Phys. Commun. 83 95
[25] Fullerton L W and Rinker G A 1976 Phys. Rev. A 13 1283
[26] Huang K N 1976 Phys. Rev. A 14 1311
[27] Angeli I and Marinova K P 2013 At. Data Nucl. Data Tables 99 69
[28] Galassi M et al GNU Scientific Library Reference Manual 3rd edn (http://www.gnu.org/software/gsl/)
[29] Goriely S, Tondeur P and Pearson J 2001 At. Data Nucl. Data Tables 77 311
[30] Johnson W R 2007 Atomic Structure Theory (Lectures on Atomic Physics) (Berlin: Springer)
[31] Latter R 1955 Phys. Rev. 99 510
[32] Sapirstein J and Cheng K T 2006 Phys. Rev. A 73 012503
[33] Cheng K T, Chen M H and Sapirstein J 2000 Phys. Rev. A 62 054501
[34] Chen M H, Cheng K T, Johnson W R and Sapirstein J 2006 Phys. Rev. A 74 042510
[35] Dzuba V A, Flambaum V V and Sushkov O P 1989 Phys. Lett. A 140 493
[36] Kramida A, Ralchenko Yu, Reader J and (NIST ASD Team) 2014 NIST Atomic Spectra Database (ver. 5.2) (Gaithersburg, MD: National Institute of Standards and Technology) (http://physics.nist.gov/asd)
[37] Dzuba V A 2008 Phys. Rev. A 78 042502
[38] Johnson W R and Sapirstein J 1986 Phys. Rev. Lett. 57 1126
[39] Dzuba V A, Flambaum V V and Sushkov O P 1989 Phys. Lett. A 141 147
[40] Dzuba V A, Flambaum V V and Ginges J S M 2002 Phys. Rev. D 66 076013
[41] Dzuba V A, Berengut J C, Flambaum V V and Roberts B 2012 Phys. Rev. Lett. 109 203003