Computational investigation of static multipole polarizabilities and sum rules for ground-state hydrogen-like ions

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Abstract

High precision multipole polarizabilities, $\alpha_\ell$ for $\ell \leq 4$ of the 1\textit{s} ground state of the hydrogen isoelectronic series are obtained from the Dirac equation using the B-spline method with Notre Dame boundary conditions. Compact analytic expressions for the polarizabilities as a function of $Z$ with a relative accuracy of $10^{-6}$ up to $Z = 100$ are determined by fitting to the calculated polarizabilities. The oscillator strengths satisfy the sum rules $\sum_i f_{0i}^{(\ell)} = 0$ for all multipoles from $\ell = 1$ to $\ell = 4$. The dispersion coefficients for the long-range H-H and H-He\textsuperscript{+} interactions are given.

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I. INTRODUCTION

The present paper reports calculations of the polarizabilities of the hydrogen atom and
electronic ions using the Dirac equation to describe the underlying dynamics. Such calcu-
lations are now topical since some atomic polarizabilities can directly impact the definitions
of two fundamental quantities, the Kelvin and the second [1]. The new generation of optical
frequency standards have reached such precision that they are sensitive to the black-body
radiation of the apparatus itself [2]. The resulting black-body radiation shift is largely de-
termined by the differences in polarizabilities of the two atomic states involved in the clock
transition. Additionally, very high precision measurements of the helium dielectric con-
stant have been recently reported [3]. In conjunction with high precision calculations of the
static dipole polarizability [4], these measurements can result in improved determinations of
Boltzmann’s constant and thus the Kelvin [3, 5].

Another reason for doing such calculations is that they can be used to verify the accuracy
of computational methods and tests of fundamental theory. The polarizabilities of the
hydrogenic ions are properties of the ground state of a set of systems that are often used
to test the fundamental principles of physics. It is rather surprising that the first explicit
calculations of the quadrupole polarizabilities of the hydrogenic ions based on the Dirac
equation have only just been reported [6].

An important advance in the topic of the dipole and higher multipole polarizabilities
was an investigation based on the Pauli approximation that gave expressions for the static
multipole polarizabilities up to $O(\alpha^2 Z^2)$ [7]. This was a generalization of an earlier work
which gave the $O(\alpha^2 Z^2)$ expression for the dipole polarizability [8]. The work on dipole
polarizabilities was extended to $(\alpha Z)^4 [9], (\alpha Z)^6 [10]$ and to all orders in terms of a general-
ized hypergeometric function [11]. Apart from a very recent calculation [6], the expressions
for the quadrupole and higher-order polarizabilities have not had independent confirmation.
There have been a number of independent calculations of the dipole polarizability and
related sum rules. Many of these investigations have been computational in nature. Drake
and Goldman derived expressions for some dipole oscillator strength sum rules as well as
performing some explicit calculations of the dipole polarizability [12] by expanding the wave
function as a linear combination of exponential type functions. Goldman [13] extended the
basis set approach to calculate the dipole polarizability of hydrogenic ions from $Z = 1$ to
$Z = 115$ using a Gauge-invariance method. A fit to the calculated polarizabilities was used
to create an $(\alpha Z)^n$ expansion of the polarizability including terms up to $(\alpha Z)^8$. There
have been a number of other computational investigations of the dipole polarizabilities of
hydrogenic ions based on Dirac equation [14–20].

The present calculations used the B-spline Galerkin method with Notre Dame (ND)
boundary conditions [19]. Other approaches to the B-spline boundary conditions have been
proposed [17, 18, 21–23]. There is at present no overwhelming reason for adopting more
complicated boundary conditions in preference to the ND boundary conditions. The B-
spline approach to atomic structure has a number of advantages [24, 25], it does not lead
to linear dependence, the basis can be made effectively complete in a finite region of space,
the details of the basis are easily adjustable and results are numerically stable. However,
lke all basis set approaches, the energy spectrum also has a sea of negative-energy states
(the Dirac sea) and it is also possible for spurious states to appear in the positive energy
spectrum [18]. These issues have been discussed extensively [17, 19, 24].

The present B-spline calculations of the multipole polarizabilities give numerical values
that are more precise than any previous calculation. Values of associated oscillator strength sum-rules are also given. The nuclear mass was set to be infinite and the point nucleus model was adopted. Values are reported for intermediate sums including the entire set of states and also for a set of calculations that omitted the negative energy states from the Dirac Sea. Analytic expressions for the polarizabilities are constructed that are accurate to a relative precision of $10^{-6}$ for $Z \leq 100$. The static multipole polarizabilities for quadrupole, octupole and hexadecupole transitions have been computed and found to be compatible with the $O(\alpha^2 Z^2)$ expressions of Kaneko et al [7]. The sum rules $\sum_i f_{\ell m}(\ell) = 0$, provide a valuable consistency check on the reliability of our calculations. Finally, the dispersion coefficients that describe the long-range interaction of the H-H and H-He$^+$ dimers in their ground states are presented. All results are reported in atomic units and the value of fine structure constant, $1/\alpha = c = 137.035 999 074$ [26] was used in all calculations reported in this work unless specifically mentioned.

II. FORMULATION

A. Dirac equation of single-electron atomic system

The single-electron Dirac equation is

$$H_D \psi(r) = E \psi(r), \quad (1)$$

$H_D$ is the Dirac Hamiltonian,

$$H_D = c \alpha \cdot p + \beta mc^2 + V(r), \quad (2)$$

where $m$ is the electron mass, $c$ is the light velocity, $p$ is the momentum operator, $\alpha$ and $\beta$ are $4 \times 4$ matrices of the Dirac operators [7].

The wavefunction for the hydrogen-like ion can be written

$$\psi(r) = \frac{1}{r} \left( \begin{array}{c} iP_{n\kappa}(r) \Omega_{\kappa m}(\hat{r}) \\ Q_{n\kappa}(r) \Omega_{-\kappa m}(\hat{r}) \end{array} \right), \quad (3)$$

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ present the larger and small components of radial wavefunction, and $\Omega_{\kappa m}(\hat{r})$ and $\Omega_{-\kappa m}(\hat{r})$ are corresponding to the angular components. The angular quantum number $\kappa$ are connected with $j$ and $\ell$,

$$\kappa = \ell(\ell + 1) - j(j + 1) - 1/4, \quad (4)$$

Substituting Eqs. (2) and (3) into Eq. (1) and separating the radial and angular components, gives the following coupled first-order differential equations for radial components $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$,

$$[V(r) + mc^2]P_{n\kappa}(r) + c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_{n\kappa}(r) = EP_{n\kappa}(r), \quad (5)$$

$$-c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_{n\kappa}(r) + [V(r) - mc^2]Q_{n\kappa}(r) = EQ_{n\kappa}(r), \quad (6)$$
In this equation \( V(r) \) is the interaction potential between the electron and nucleus, 

\[
V(r) = -\frac{Z}{r},
\]

with \( Z \) being the number of nuclear charges.

In order to compare with non-relativistic calculations, we replace the energy \( E \) by \( \varepsilon = E - mc^2 \), and the radial Dirac equation can be written as matrix style,

\[
\begin{pmatrix}
V(r) & c\left(\frac{d}{dr} - \kappa\right) \\
-c\left(\frac{d}{dr} + \kappa\right) & -2mc^2 + V(r)
\end{pmatrix}
\begin{pmatrix}
P_{\kappa n}(r) \\
Q_{\kappa n}(r)
\end{pmatrix} = \varepsilon
\begin{pmatrix}
P_{\kappa n}(r) \\
Q_{\kappa n}(r)
\end{pmatrix}.
\]

(B. B-spline Galerkin method)

The radial wavefunctions \( P_{\kappa n}(r) \) and \( Q_{\kappa n}(r) \) are expanded in a \( N \)-dimensional basis of B-splines of order \( k \),

\[
P(r) = \sum_{i=1}^{N} p_i B^k_i(r),
\]

\[
Q(r) = \sum_{i=1}^{N} q_i B^k_i(r),
\]

where the subscripts \( n, \kappa \) have been omitted from the functions \( P_{\kappa n}(r) \) and \( Q_{\kappa n}(r) \) for notational simplicity. The function \( B^k_i(r) \) only take nonzero values for the knot intervals \( t_i \leq r \leq t_{i+k} \). The normalization condition is

\[
\int_{0}^{\infty} [P^2(r) + Q^2(r)]dr = 1.
\]

The details of the B-splines and ND boundary conditions have been discussed in detail elsewhere \[18, 19\]. The large and small radial components are independently expanded in a B-spline basis with the boundary conditions, \( P(R) = Q(R) \) and \( P(0) = 0 \), where \( R \) is the radius of confining cavity.

B-splines of \( k = 9 \) order were used with the endpoints of multiplicity 9. An exponential knot distribution for the B-splines is adopted, e.g.

\[
t_{i+k-1} = R \times \frac{\exp(\gamma(\frac{i-1}{N_1-1})) - 1}{\exp(\gamma) - 1},
\]

where \( i = 1, 2, \ldots, N_1 \) and \( N_1 = N - k + 2 \) being the maximal value of \( i \). The exponential knot parameter \( \gamma \) depends on the radius of confining cavity \( R \),

\[
\gamma = G(Z) \times R.
\]

The function \( G(Z) \) for \( Z \geq 2 \) satisfies the recurrence relation

\[
G(Z) = G(Z - 1) + \frac{0.055}{Z},
\]
where $G(1) = 0.055$ is an optimized value for the hydrogen atom. The confining cavity radius $R$ (which is different for different $Z$) was chosen to reproduce the exact ground-state energy $[27]$ of the hydrogen-like ions to at least 20 significant digits

$$
\varepsilon_n^\text{Exact} = c^2 \left[ 1 + \frac{(\alpha Z)^2}{[n - |\kappa| + \sqrt{\kappa^2 - (\alpha Z)^2}]^2} \right]^{-1/2} - c^2 .
$$

where $n$ is the main quantum number.

### C. Polarizabilities for the single-electron atoms

In a weak external electric field, the static $2\ell$-pole polarizability for an atom is usually defined in terms of a sum over all intermediate states including the continuum,

$$
\alpha_\ell = \sum_i \frac{f^{(\ell)}_{gi}}{(E_i - E_g)^2} .
$$

The initial state, $\psi_g(r)$, with energy, $E_g$, is excluded from the summation over $i$. The $2\ell$-pole oscillator strength $f^{(\ell)}_{gi}$ from ground state $g$ to excited state $i$ is defined

$$
f^{(\ell)}_{gi} = \frac{2(E_i - E_g)|\langle \psi_i(r) | r^{\ell} | \psi_g(r) \rangle|^2}{(2\ell + 1)(2j_g + 1)},
$$

where $j_g$ is the total angular momentum for the ground-state. The wavefunction and energy of the excited states are $\psi_i(r)$ and $E_i$. $C^{(\ell)}(\hat{r})$ is the $\ell$-order spherical tensor.

Using Eq. (3), the radial and angular parts of matrix element in the Eq. (17) are

$$
\langle \psi_g(r) | r^{\ell} | \psi_i(r) \rangle = \int_0^\infty r^{\ell} [P_g(r)P_i(r) + Q_g(r)Q_i(r)] dr ,
$$

$$
\langle \Omega_{\kappa_g}(\hat{r}) | C^{(\ell)}(\hat{r}) | \Omega_{\kappa_i}(\hat{r}) \rangle = (-1)^{j_g + \frac{\ell}{2}} \sqrt{(2j_g + 1)(2j_i + 1)} \times \left( \begin{array}{ccc} j_g & j_i & \ell \\ -1/2 & 1/2 & 0 \end{array} \right).
$$

Polarizabilities that are computed including both the physical states and negative energy states of the Dirac sea in Eq. (16) are denoted by $\alpha_\ell^\pm$. Polarizabilities that are computed by omitting the negative energy states of the Dirac Sea in Eq. (16) are denoted by $\alpha_\ell^\mp$. The states of the Dirac sea are energetically distinct from the physical states. The polarizabilities computed using the $O(\alpha^2 Z^2)$ expressions of [17] are denoted as $\alpha_\ell^K$.

The polarizabilities can be expanded as a series in powers of $(\alpha Z)^2$. The series is written

$$
\alpha_\ell^R = \alpha_\ell^{\text{NR}} \left[ 1 + \sum_{i=1}^n \lambda_{2i}(\alpha Z)^{2i} \right],
$$

where the non-relativistic multipole polarizabilities, $\alpha_{\ell}^{\text{NR}}$, for the ground-state hydrogen-like ions, which have the exact values [28]

$$
\alpha_\ell^{\text{NR}} = \frac{(2\ell + 2)!(\ell + 2)}{\ell(\ell + 1)2^{2\ell+1}Z^{2\ell+2}} .
$$


D. Oscillator strength sum rules

There are a number of oscillator strength sum rules besides those which define the multipole polarizabilities. We make the definition

\[ S_\ell(n) = \sum_i f^{(\ell)}_{gi} (E_i - E_g)^n \]  

(22)

The expression with \( \ell = 1 \) and \( n = -2 \) is the dipole polarizability, The case when \( \ell = 1 \) and \( n = 0 \) is called the Thomas-Reiche-Kuhn (TRK) sum rule. In the non-relativistic calculation, \( S_1(0) \) should be equal to the number of the electrons. The case with \( \ell = 1 \) and \( n = -3 \) is related to the non-adiabatic dipole polarizability. One finds that \( S_1(-3) = 43/(4Z^6) \) for non-relativistic hydrogenic atoms. The \( S_1(-1) \) coefficient is related to the long-range atom wall dispersion coefficient. One finds that \( S_1(-1) = 2/Z^2 \) for non-relativistic hydrogenic atoms. The relativistic sum rules are useful in testing the completeness of basis sets for variational representations of the Dirac spectrum and set a foundation for testing other methods.

As with the polarizabilities, the sum-rules can be evaluated by summing over all states, or just the positive energy states. Sum rules that are computed including both positive and negative energy states in Eq. (22) are denoted by \( S_\ell^\pm(n) \). Sum rules that omit the states from the negative energy sea from the sum are denoted by \( S_\ell^+(n) \).

III. RESULTS AND DISCUSSIONS

A. Polarizabilities and sum rules for hydrogen

![Graph](image)

FIG. 1: (color online). The convergence of ground-state energy (a.u.) relative to the exact Dirac equation energy of the hydrogen ground state. The number of B-spline basis functions is \( N \), while the radius of confining cavity is \( R = 400 \) a.u.

The difference of the B-spline ground-state energy from the exact energy given by Eq. (15) (this is \(-0.500 000 656 596 553 596 900 786 4298 \) a.u.) as a function of the dimension of the B-spline basis is plotted in Fig[1]. This calculation was performed with a confinement radius of \( R = 400 \) a.u.. This ensures that none of the atomic sum rules reported in this paper are
TABLE I: The convergence of the static multipole polarizabilities $\alpha_\ell^\pm$ (units of a.u.) for the hydrogen atom ground state as the dimension, $N$, of the B-spline basis set was increased. The radius of the confining cavity is $R = 400$ a.u.

| $N$  | $\alpha_1^+$  | $\alpha_2^+$  | $\alpha_3^+$  | $\alpha_4^+$ |
|------|---------------|---------------|---------------|---------------|
| 100  | 4.499 751 495 18 | 14.998 829 821 | 131.2379      | 2126.028 674 4992 |
| 150  | 4.499 751 495 177 64 | 14.998 829 822 856 41 | 131.237 821 447 844 63 | 2126.028 674 499 128 81 |
| 200  | 4.499 751 495 177 639 27 | 14.998 829 822 856 441 76 | 131.237 821 447 844 661 | 2126.028 674 499 128 81 |
| 250  | 4.499 751 495 177 639 267 48 | 14.998 829 822 856 441 70 | 131.237 821 447 844 661 | 2126.028 674 499 128 81 |
| 300  | 4.499 751 495 177 639 267 398 1 | 14.998 829 822 856 441 699 67 | 131.237 821 447 844 662 144 | 2126.028 674 499 128 81 |
| 350  | 4.499 751 495 177 639 267 396 1 | 14.998 829 822 856 441 699 61 | 131.237 821 447 844 662 150 7 | 2126.028 674 499 128 81 |
| 400  | 4.499 751 495 177 639 267 396 02 | 14.998 829 822 856 441 699 608 | 131.237 821 447 844 662 151 0 | 2126.028 674 499 128 81 |

TABLE II: The comparison of dipole sum rules, $S_1^\pm(n)$ and $S_1^\pm(n)$, for the H(1s) ground state. The exact expressions of sum rule are also presented in the fourth-column with $\gamma_1 = \sqrt{r^2 - \alpha^2}Z^2$ [12]. The non-relativistic values are in the column $S_1^{NR}(n)$. The value of $S_1^\pm(0)$ is not stable and gets smaller as the B-spline basis dimension is increased. The notation $a[b]$ means $a \times 10^b$.

| Sum rule | $S_1^+(n)$ | $S_1^-(n)$ | $S_1^{NR}(n)$ | $S_1^{exact}(n)$ | $\Delta S_1(n)/S_1^{exact}(n)$ |
|----------|------------|------------|---------------|----------------|-------------------------------|
| $S_1(-3)$ | 10.749 260 777 454 106 9 | 10.749 260 777 454 125 8 | 10.75 | $(\gamma_1 + 1)(2\gamma_1 + 1)$ | 7[-19] |
| $S_1(-2)$ | 4.499 751 495 886 496 76 | 4.499 751 495 177 639 27 | 4.50 | $3\gamma_1^2$ | 3[-29] |
| $S_1(-1)$ | 0.999 995 631 350 807 45 | 1.0 | 2 | $2/\alpha^2$ | 2[-18] |
| $S_1(0)$ | 6.666 563 210 276 996 94 | 3.755 773 608 441 865 7y[4] | 2 | $\gamma_1/2 \alpha^2$ | 2[-18] |
| $S_1(1)$ | 3.755 773 608 441 865 7y[4] | 3 | $2/\alpha^2$ | $3\gamma_1^2 + 4/\alpha^2$ | $4/\alpha^2$ |
| $S_1(2)$ | 0.999 995 631 350 807 45 | $-1.410 595 609 170 789$ | 2 | $3\gamma_1^2 + 4/\alpha^2$ | $3\gamma_1^2 + 4/\alpha^2$ |
| $S_1(3)$ | 5.298 0179 899 713 | 5.298 0179 899 713 | 2 | $-2/\alpha^2$ | $-2/\alpha^2$ |

influenced by the size of the confinement radius. The energy was converged to 25 significant digits for a basis with $N = 400$.

Table I shows the convergence of the static multipole polarizabilities, $\alpha_\ell^\pm$, for the H(1s) state as the dimension of the B-spline basis was increased from $N = 100$ to $N = 400$. The radius of confining cavity is $R = 400$ a.u. The static dipole polarizability $\alpha_1^\pm$, is computed to a precision of 22 digits. The higher-order polarizabilities $\alpha_2^\pm$, $\alpha_3^\pm$, and $\alpha_4^\pm$ have not achieved the same degree of precision, but are still computed to a precision of 21, 20, and 20 effective figures respectively. The present $\alpha_1^\pm = 4.499 751 495 177 639 267 396 02$ a.u. is $4 \times 10^{-11}$ a.u. larger than the result $4.499 751 495 142 92$ a.u. of Goldman [13]. This is due to the different fine structure constant used. When the fine-structure constant $\alpha$, is set to the value used by Goldman, namely $1/\alpha = 137.035 999 074$, the B-spline polarizability changed to $\alpha_1^\pm = 4.499 751 495 142 916$ a.u. This is in perfect agreement with that of Goldman. All hydrogen atom sum-rules reported from now on use the $N = 400, R = 400$ a.u. B-spline basis.

Exact expressions exist for a number of the dipole sum rules given by Eq. (22). For example, the expressions for the exact non-relativistic electric-dipole sum rules $S_1(n)$ have been derived for $n = -5, -4, \ldots, 2$ [30, 33]. The non-relativistic dipole sum-rule diverges for $n \geq 3$. Expressions for some dipole sum rules for the Dirac hydrogen atom have been given by Drake and Goldman [12]. The Dirac equation sum rules were derived by using close
TABLE III: The comparison of the H(1s) static multipole polarizabilities and sum rules with and without the negative energy states. Values for $S^\ell_+(0)$ are not numerically stable and tend to decrease as the basis is enlarged. The notation $a[b]$ means $a \times 10^b$.

| Sum rule | $S^\ell_+$ | $S^\ell_{NR}$ | Non-relativistic |
|----------|------------|---------------|-----------------|
| $S_2(−3)$ | 26.747 582 450 922 508 1 | 26.747 582 450 922 621 3 | 26.750 |
| $S_2(−2)$ | 14.998 829 827 109 609 3 | 14.998 829 822 856 441 7 | 15.0 |
| $S_2(−1)$ | 8.999 384 961 848 033 62 | 8.999 544 703 263 054 54 | 9.0 |
| $S_2(0)$ | 5.999 605 961 023 935 20 | $−1[−28]$ | 6.0 |
| $S_2(1)$ | 4.799 754 122 244 844 66 | 2.253 393 826 733 66[5] | 4.80 |
| $S_2(2)$ | 5.598 084 401 231 297 2 | $−8.463 168 026 239 51[9]$ | 5.60 |
| $S_2(3)$ | 20.043 653 259 626 | 3.178 616 122 279 928[14] | 20.80 |
| $S_3(−3)$ | 204.041 400 069 326 002 | 204.041 400 069 327 276 | 204.06250 |
| $S_3(−2)$ | 131.237 821 495 692 427 | 131.237 821 447 844 662 | 131.250 |
| $S_3(−1)$ | 89.992 366 277 948 754 1 | 89.994 163 347 335 786 6 | 90.0 |
| $S_3(0)$ | 67.494 445 945 723 638 3 | 6[$−24]$ | 67.50 |
| $S_3(1)$ | 57.851 751 717 231 297 2 | 2.535 018 531 367 228 21[6] | 442 | 61.742857 |
| $S_3(2)$ | 61.704 978 988 083 113 1 | $−9.520 821 387 020 49[10]$ | 442 | 61.7857142 |
| $S_3(3)$ | 100.225 824 655 056 308 | 3.575 836 136 347 471[15] | 725 | 100.2857142 |
| $S_4(−3)$ | 304.342 638 220 497 017 | 304.342 638 220 494 85 | 304.3687 50 |
| $S_4(−2)$ | 2126.028 675 392 279 56 | 2126.028 674 499 128 83 | 2126.25 |
| $S_4(−1)$ | 1574.848 826 948 754 1 | 1574.848 826 948 754 1 | 1575.0 |
| $S_4(0)$ | 1259.880 083 503 994 17 | 9[$−19$] | 1260.0 |
| $S_4(1)$ | 1119.885 837 666 203 30 | 4.731 967 094 641 248 23[7] | 1120.0 |
| $S_4(2)$ | 1159.848 826 903 744 95 | $−1.777 189 196 500 64[12]$ | 1160.0 |
| $S_4(3)$ | 1530.311 794 804 461 | 6.674 763 648 090 144[16] | 452 | 1530.66666666 |

to sum over the complete set of positive and negative energy states and the expressions are given in Table III. The Dirac equation sum-rule for $S_1(3)$ is convergent due to cancellations between the terms with positive and negative energies.

Table III compares the dipole sum rules of the H(1s) with and without the contributions of the states in the negative energy sea. All the digits listed are converged with respect to further enlargement of the B-spline basis. The sum-rules, $S^\ell_+(0)$, $S^\ell_+(1)$ and $S^\ell_+(2)$, agree with the exact expressions to better than 15 digits. Agreement is not so good for $S_1(3)$ but in this case the sum is more sensitive to terms that occur at larger positive and negative energies. There was no evidence of convergence for $S_1(3)$ when the states of the negative energy sea were omitted from intermediate sum. This is consistent with the non-relativistic result of Lamm and Szabo [34].

The value $S^\ell_+(0)$, which omits the states from the Dirac sea, is close to the non-relativistic value of nuclear charge $Z = 1$. Upon making the substitution $\langle p^2 \rangle = Z^2$ in existing expressions [35, 36], we obtain the result

$$S^\ell_{Levinger}(0) = 1 − \frac{5\alpha^2 Z^2}{6} + \ldots , \quad (23)$$

Evaluating this expression for $Z = 1$ gives, $S_1(0) = 0.999 955 6238$, which is only $8 \times 10^{-9}$ different from the B-spline evaluation. The degree of difference between $S^\ell_{NR}(n)$ and $S^\ell_+(n)$ gets larger as $n$ increases. The difference is $3.0\%$ for $S_1(2)$.

The contribution that the negative-energy states make to the dipole sum rules depends on $n$. The negative-energy states of the Dirac sea contribute less than $2 \times 10^{-5}$ to $S^\ell_+(−1)$, $2 \times 10^{-10}$ to $S^\ell_+(−2)$, and $2 \times 10^{-15}$ to $S^\ell_+(−3)$. This is not surprising. The negative energy states are located at energies of order $−2c^2$. So the contributions of the negative energy states decrease as $n$ in Eq. (22) becomes increasingly negative. Conversely, the differences between the $S^\ell_+(n)$ and the $S^\ell_{Levinger}(n)$ sum rules can be expected to increase as $n$ increases.
Table IV shows that this indeed does happen. The difference between $S_1^\pm(2)$ and $S_1^+(2)$ is nine orders of magnitude.

Table III gives the sum rules for the higher-order multipoles for the hydrogen-atom ground state. The $S_2(-2), S_3(-2),$ and $S_4(-2)$ are the multipole polarizabilities $\alpha_2, \alpha_3,$ and $\alpha_4$ respectively. The sum-rules, $S_\ell^+(n)$, omitting the states from the Dirac sea are within 0.1% of the non-relativistic values with the exception of $S_2(3)$. This is also true for the sum-rules, $S_\ell^+(n)$, with $n < 0$ that also include the Dirac sea.

The most striking results from Table III are the $S_\ell^+(0)$ sum-rules which do not exceed $10^{-18}$. Levinger et al. [35] have pointed out that the Dirac Hamiltonian involves terms linear in the particle momentum $\mathbf{p}$ and that as a consequence the Bethe sum rule for $\exp(i\mathbf{q} \cdot \mathbf{r})$ should be identically zero. The expansion of $\exp(i\mathbf{q} \cdot \mathbf{r})$ implicitly involves dipole, quadrupole and octupole matrix elements. Therefore, it is expected that $S_\ell(0) = 0$ for all $\ell$.

The contributions of the negative-energy Dirac Sea to the $S_\ell^+(n)$ sum-rules are actually greater than the contributions from the physical states for $n \geq 1$. They exceed the contribution from the physical states by amounts from 4 to 14 orders of magnitude.

B. Polarizabilities for the hydrogen isoelectronic series

Table IV presents the static dipole polarizabilities for a number for hydrogen-like ions in their ground-state. All the digits listed in this table are converged with respect to further enlargement of the B-spline basis. In order to facilitate comparison of the present polarizabilities with those of Goldman [13], we repeated the calculations but used the same speed of light $c = 137.035 \times 10^5$ (in atomic units) as Goldman. The agreement
with the polarizabilities of Goldman could hardly have been better. At \( Z = 10 \) we got \( \alpha_1^{\pm} = 4.475\,164\,357\,157\,0908 \times 10^{-4} \) a.u., in agreement with all published digits of Goldman. The same is true for the polarizability at \( Z = 90 \), namely \( 3.944\,093\,496\,045\,4043 \times 10^{-8} \) a.u. This level of agreement was achieved for all values of \( Z \) from 1 to 100. The only disagreements amounted to \( \pm 1 \) in the last significant digit reported by Goldman [13].

FIG. 2: (color online). The impact of relativistic effects on the multipole polarizabilities for the hydrogen isoelectronic series. The ratio \( (\alpha_\ell^{\pm} - \alpha_\ell^{NR})/\alpha_\ell^{NR} \) is plotted.

The higher-order polarizabilities, \( \alpha_\ell^{\pm} \) of the ground-states of some selected hydrogen-like ions are presented in Table V. All the reported digits are insensitive to further enlargement in the B-spline basis. Fig. 2 shows the influence of relativistic effect on multipole polarizabilities. The relativistic effect becomes larger as the nuclear charge, \( Z \), is increased. The relative size of the relativistic effect is smallest for the dipole polarizability and largest for \( \alpha_4 \).

FIG. 3: (color online). Plot of \( 10^9 \Delta \alpha_1/Z^2 \) as a function of nuclear charge, \( Z \).

The difference of the \( \alpha_1^{\pm} \) and \( \alpha_1^{+} \) polarizabilities from the Kaneko polarizabilities are illustrated in Fig. 3. We define \( \Delta \alpha_1^{\pm} = (\alpha_1^{\pm} - \alpha_1^{K}) \) with a similar relation used to define \( \Delta \alpha_1^{+} \). Fig. 3 plots \( 10^9 \Delta \alpha_1 \) as a function of \( Z \). These are seen to go to a constant value as
From Eq. (20) we deduce

\[
\Delta \alpha_1^\pm = 9 \frac{\lambda_2 + 28}{27 Z^4} \left( \alpha Z \right)^2 + O(\alpha^4 Z^4).
\]  

(24)

This expression can only go to a constant in the \( Z \to 0 \) limit when \( \lambda_2 = -\frac{28}{27} \). Fig. 3 demonstrates that \( \alpha_1^\pm, \alpha_1^+, \) and \( \alpha_1^K \) are equal to order \( O(\alpha^2 Z^2) \). The different \( Z \to 0 \) asymptotes for \( \Delta \alpha_1^\pm \) and \( \Delta \alpha_1^+ \) indicate that the \( O(\alpha^4 Z^4) \) terms are different for \( \alpha_1^\pm \) and \( \alpha_1^+ \).

**FIG. 4:** (color online). Plot of \( 10^{15} (\alpha_1^\pm - \alpha_1^{\text{Zon}}) / Z^2 \) as a function of nuclear charge, \( Z \).

Expressions for \( \alpha_1^\pm \) giving terms to \( O(\alpha^4 Z^4) \) \[9\], \( O(\alpha^6 Z^6) \) \[10\] and to all orders \[11\] have been derived. The \( O(\alpha^4 Z^4) \) expression of Zon \[9\] is

\[
\alpha_1^{\text{Zon}} = \frac{9}{2 Z^4} \left[ 1 - \frac{28}{27} (\alpha Z)^2 + \frac{31 + 2 \pi^2}{432} (\alpha^4 Z^4) + \ldots \right].
\]  

(25)

Figure 4 plots \( 10^{15} (\alpha_1^\pm - \alpha_1^{\text{Zon}}) / Z^2 \) as a function of \( Z \). The \( Z \to 0 \) limit of this difference demonstrates that the present calculations are in agreement with the analytic expression to \( O(\alpha^4 Z^4) \). This provides a mutual validation of the B-spline calculations and the analytic expressions.

Figure 5 plots \( 10^9 Z^4 \Delta \alpha_3 \) as a function of \( Z \). These are seen to go to a constant value as \( Z \to 0 \). By an analysis similar to that performed for the dipole polarizability, one can deduce that \( \alpha_3^\pm, \alpha_3^+, \) and \( \alpha_3^K \) are equal to order \( O(\alpha^2 Z^2) \). The different \( Z \to 0 \) asymptotes for \( \Delta \alpha_3^\pm \) and \( \Delta \alpha_3^+ \) indicate that \( O(\alpha^4 Z^4) \) terms are different for \( \alpha_3^\pm \) and \( \alpha_3^+ \).

The analysis demonstrating that the differences between \( \alpha_3^\pm \) and \( \alpha_3^+ \) only appear at \( O(\alpha^4 Z^4) \) has already been reported \[6\]. It has previously been shown that these polarizabilities are agreement with the Kaneko \( O(\alpha^2 Z^2) \) \[6\]. It is also possible to plot \( 10^9 Z^6 \Delta \alpha_4 \) as a function of \( Z \) giving plots similar to Figs. 3 and 5. This demonstrates that \( \alpha_4^\pm \) and \( \alpha_4^+ \) agree with \( \alpha_4^K \) at the \( O(\alpha^2 Z^2) \) level and the difference between \( \alpha_4^\pm \) and \( \alpha_4^+ \) occurs at the \( O(\alpha^4 Z^4) \) order.

**C. Sum-rules for the hydrogen isoelectronic series**

The non-relativistic TRK sum-rule, \( S_1(0) \) gives a value of unity \[30, 33, 37\] for all hydrogen-like atoms and ions. However, \( S_1^+(0) \) is exactly zero while the sum-rule, \( S_1^+(0) \)
TABLE V: Relativistic multipole polarizabilities (in a.u.) for the ground states of the hydrogen isoelectronic series. All the figures listed are accurate. The notation \(a \times 10^b\) means \(a \times 10^b\).

| \(Z\) | \(a_2^+\) | \(a_3^+\) | \(a_4^+\) |
|-------|-----------|-----------|-----------|
| 1     | 14.998 829 822 856 441 699 | 131.237 821 447 844 662 | 2126.028 674 499 128 83 |
| 2     | 0.234 301 867 935 791 210 0 | 0.512 505 037 523 770 47 | 2.075 551 540 612 051 9 |
| 5     | 9.581 285 372 324 045 92 | 3.352 210 607 878 016 2 | 2.171 618 426 945 541 1 |
| 10    | 1.488 319 833 913 411 04 | 1.300 352 899 787 624 [-6] | 2.104 187 645 750 314 [-7] |
| 15    | 1.293 852 351 688 892 4 | 5.014 877 480 967 07 [-8] | 3.601 503 954 501 5 |
| 20    | 2.271 146 583 050 793 [-7] | 4.938 640 072 269 2 | 1.991 062 443 017 [-10] |
| 25    | 5.847 845 585 737 33 [-8] | 8.110 859 162 392 [-10] | 2.087 370 771 99 [-11] |
| 30    | 1.915 515 761 865 58 [-8] | 1.837 296 630 650 [-10] | 3.273 123 521 7 [-12] |
| 35    | 7.397 473 245 589 1 [-9] | 5.186 973 978 69 [-11] | 6.763 105 560 [-13] |
| 40    | 3.218 326 876 369 0 [-9] | 1.717 671 116 72 [-11] | 1.707 062 443 017 [-12] |
| 45    | 1.531 561 509 916 7 [-9] | 6.415 324 043 1 [-12] | 5.011 809 33 [-14] |
| 50    | 7.812 859 401 235 [-10] | 2.630 602 571 9 [-12] | 1.654 931 37 [-14] |
| 55    | 4.210 472 655 409 [-10] | 1.616 555 467 5 [-12] | 5.999 556 2 [-15] |
| 60    | 2.371 147 053 044 [-10] | 5.443 579 080 [-13] | 2.345 208 2 [-15] |
| 65    | 1.383 617 655 412 [-10] | 2.677 457 400 [-13] | 9.748 095 [-16] |
| 70    | 8.309 087 512 23 [-11] | 1.369 821 733 [-13] | 4.261 037 [-16] |
| 75    | 5.106 469 950 92 [-11] | 7.235 969 19 [-14] | 1.940 914 [-16] |
| 80    | 3.196 013 748 39 [-11] | 3.921 694 89 [-14] | 9.141 67 [-17] |
| 85    | 2.028 253 121 49 [-11] | 2.168 463 36 [-14] | 4.421 83 [-17] |
| 90    | 1.299 794 490 85 [-11] | 1.216 900 77 [-14] | 2.182 71 [-17] |
| 95    | 8.376 878 675 0 [-12] | 6.895 117 0 [-15] | 1.092 81 [-17] |
| 100   | 5.405 559 183 5 [-12] | 3.923 335 2 [-15] | 5.514 2 [-18] |

is almost equal to 1. The appropriate method to choose for the evaluation of the TRK sum rule has generated considerable discussion [12, 35, 36, 38–43]. Table VI compares the present B-spline values of \(S_1^+ \) and compares them against the earlier calculation of Drake and Goldman [12]. Keeping in mind the limited precision of the earlier calculation, the agreement with the Drake and Goldman calculation is perfect.

Figure 6 shows \(\Delta S_1(0) = S_1^+(0) - S_1^{+\text{Levinger}}(0)\), plotted as a function of \(Z\). It is noticed that \(\Delta S_1(0)/Z^4\) goes to a constant as \(Z \to 0\). This demonstrates that the present \(S_1^+ \) is in agreement with the expression of Levinger to order \(O(\alpha^2 Z^2)\). It also demonstrates that the next term in the expression for \(S_1^+ \) occurs at the \(O(\alpha^4 Z^4)\) level. The near linear behaviour of \(\Delta S_1(0)/Z^4\) at small \(Z\) indicates that the expansion for \(S_1^+ \) contains a term of \(O(\alpha^5 Z^5)\).

While the B-spline calculations of \(S^+(0)\) are compatible with \(O(\alpha^2 Z^2)\) expressions [35, 36], they cannot be reconciled with the \(O(\alpha^4 Z^4)\) expression of Cohen. A simple analysis near \(Z = 0\) suggests that

\[
S_1^+(0) \approx 1 - \frac{5\alpha^2 Z^2}{6} + 2.71 \alpha^4 Z^4 - 6\alpha^5 Z^5 + O(\alpha^6 Z^6) .
\]
FIG. 5: (color online). Plot of $10^9 Z^4 \Delta \alpha_3$ as a function of nuclear charge, $Z$.

TABLE VI: Comparison of the $S_1^+(0)$ sum rules. All digits are stable with respect to further enlargement of the B-spline basis.

| $Z$ | Present                  | Ref. [12]      |
|-----|--------------------------|----------------|
| 1   | 0.999 955 631 350 807    | 0.999 9556     |
| 2   | 0.999 822 612 102 297    |                |
| 5   | 0.998 894 823 187 627    |                |
| 10  | 0.995 622 481 263 678    | 0.995 62       |
| 15  | 0.990 287 581 618 103    |                |
| 20  | 0.983 023 671 163 131    | 0.9830         |
| 25  | 0.973 973 703 862 452    |                |
| 30  | 0.963 278 628 607 378    | 0.9633         |
| 35  | 0.951 070 787 251 835    |                |
| 40  | 0.937 470 188 595 043    | 0.9375         |
| 45  | 0.922 582 481 520 977    |                |
| 50  | 0.906 497 887 620 449    | 0.9065         |
| 60  | 0.871 018 387 592 671    | 0.8710         |
| 70  | 0.831 424 017 561 149    | 0.8314         |
| 80  | 0.787 815 483 542 815    | 0.7878         |
| 90  | 0.739 933 345 752 064    | 0.7399         |
| 100 | 0.686 987 401 548 771    | 0.69           |

It has not been possible to reconcile the coefficient of 2.71 with Eq. (8) of Cohen [36]. But it is unclear how to interpret $\langle p^4 \rangle$ of Eq. (8) in [36]. The plot of $S_1^+(0)$ depicted in Fig. 3 of [36] is certainly compatible with the present B-spline calculation. However, Fig. 3 of [36] plots the $O(\langle p^2 \rangle)$ approximation to $S_1^+(0)$ and this is certainly not equal to $1 - \frac{5\alpha^2 Z^2}{6}$.

Figure 7 shows the difference

$$\Delta S_1(n) = S_1^+(n) - S_1^+(n),$$

plotted against $Z$ for $n = -1$ and $n = -3$. It is noticed that $\lim_{Z \to 0} \Delta S_1(-1)$ and $\Delta S_1(-3)$
both go to a constant as $Z \to 0$. Figure 5 established that $\Delta S_1(-2)$ also has the same $Z \to 0$ limiting behaviour. Writing either of the $S_1(n)$ in the form

$$S_1(n) = S_{1NR}^+(n) \left( 1 + c_2 \alpha^2 Z^2 + c_4 \alpha^4 Z^4 + \ldots \right),$$

(29)

allows one to deduce that the $c_2$ coefficients are different for $S_1^+(-1)$ and $S_1^+(-1)$ since $S_{1NR}^+(1) = 2/Z^2$. However, one deduces that the $c_2$ and $c_4$ coefficients are actually the same for $S_1^+(-3)$ and $S_1^+(-3)$ since $S_{1NR}^+(-3) = 43/(4Z^6)$.

D. Analytic expressions for the multipole polarizabilities of hydrogen-like ions

Analytic expressions were derived for $\alpha_\ell^\pm$ by performing a least squares fit of the polarizabilities to Eq. (20). The polarizabilities were divided by the non-relativistic values prior to the fit. The value of $\lambda_2$ was fixed at the values of Kaneko for $\ell = 1, 2$ and 3. The $\lambda_2$ value for $\ell = 4$ was determined by evaluating Eq. (36) of Ref. [7]. The value of $\lambda_4$ for $\alpha_1^\pm$ was set to the value from Zon [9]. Table VII lists the numerical values of $\lambda_{2i}$ coming from the
fit. These coefficients give a more precise representation of the exact dipole polarizabilities than two previous representations [12, 13]. The expressions for the quadrupole and octupole polarizabilities are novel.

The quality of the fit to the B-spline $\alpha_\ell^\pm$ can be seen from Fig. 8. The quality of the fits are of very high accuracy at the smaller values of $Z$. This occurs since the leading $\lambda_2 \alpha_2^2 Z^2$ term uses the exact value of $\lambda_2$. The quality of the fit is degraded at larger values of $Z$. However, the maximum relative error in the analytic expressions only exceeds one part per million for values of $Z$ close to 100.

Equation (20) was also used to create an analytic expression for $\alpha_4^\pm$. In this case, the $\lambda_{2i}$

FIG. 8: (color online). Relative difference between $\alpha_\ell^\pm$ and the fits to this using Eq. (20) as a function of nuclear charge, $Z$.

TABLE VII: The Eq. (20) fits to the multipole polarizabilities of hydrogen isoelectronic series ground states.

| Term | $\alpha_1^\pm$ [13] | $\alpha_1^\pm$ | $\alpha_2^\pm$ | $\alpha_3^\pm$ | $\alpha_4^\pm$ |
|------|-----------------|---------------|---------------|---------------|---------------|
| $\alpha_{NR}$ | $\frac{9}{2 Z^4}$ | $\frac{28}{27}$ | $\frac{28}{27}$ | $\frac{879}{600}$ | $\frac{5123}{2940}$ |
| $\lambda_2$ | $-\frac{28}{27}$ | $\frac{879}{600}$ | $\frac{5123}{2940}$ | $17010$ |
| $\lambda_4$ | 0.117 451 87(1) | 0.117 451 870 668 402 | 0.502 471 315 | 0.854 144 263 | 1.177 235 432 |
| $\lambda_6$ | 0.007 692 784 | $-0.014 151 521$ | $-0.102 874 518$ | $-0.228 232 960$ |
| $\lambda_8$ | 0.001 482(1) | $-0.003 271 333$ | $0.002 052 103$ | $0.001 433 636$ | $0.001 629 938$ |
| $\lambda_{10}$ | $-0.006 117 861$ | $-0.000 261 805$ | $0.001 019 239$ | $-0.000 189 306$ |
| $\lambda_{12}$ | $-0.013 528 604$ | $-0.003 271 333$ | $0.002 052 103$ | $0.001 433 636$ | $0.001 629 938$ |

Equation (20) was also used to create an analytic expression for $\alpha_4^\pm$. In this case, the $\lambda_{2i}$...
TABLE VIII: The second-order dispersion coefficients (in a.u.) for the H(1s)-H(1s) and H(1s)-He\(^+\)(1s) systems. Results are given for the sum rules evaluated with and without the states of the Dirac sea. All tabulated digits are accurate. The notation \(a[b]\) means \(a \times 10^b\).

| \(C_n^\pm\) | \(C_n^\pm\) | Non-relativistic |
|------------|------------|----------------|
| \(C_6\)   | 6.498 392 250 007 09 | 6.498 392 245 754 06 | 6.499 026 705 405 84 |
| \(C_8\)   | 1.243 840 307 694 35[2] | 1.243 840 306 577 93[2] | 1.243 990 835 836 22[2] |
| \(C_{10}\) | 3.285 370 791 861 60[3] | 3.285 370 788 289 10[3] | 3.285 828 414 967 42[3] |
| \(H(1s)-H(1s)\) | | | |
| \(C_6\)   | 0.657 548 755 759 311 | 0.657 548 758 416 787 | 0.657 716 656 238 770 |
| \(C_8\)   | 8.335 406 342 724 22 | 8.335 406 384 081 09 | 8.337 819 589 166 31 |
| \(C_{10}\) | 1.588 773 716 759 79[2] | 1.588 773 725 479 53[2] | 1.589 267 575 526 71[2] |
| \(H(1s)-He^+(1s)\) | | | |

IV. DISPERSION COEFFICIENTS

The long-range dispersion interaction between two spherically symmetric atoms can be written

\[
V_{\text{disp}}(R) \sim - \sum_{n=3}^{\infty} \frac{C_{2n}}{R^{2n}},
\]

(30)

The dispersion coefficients, \(C_{2n}\), can be evaluated using oscillator strength sum rules. The explicit expression is

\[
C_{2n} = \sum_{\ell_i=1}^{n-2} \sum_{\ell_j=1}^{n-2} \delta_{\ell_i+\ell_j,n-1} \frac{(2n-2)!}{4(2\ell_i)!(2\ell_j)!} \times \sum_{ij} f_{A,gi}^{(\ell_i)} f_{B,gj}^{(\ell_j)} \frac{\varepsilon_{A,gi} \varepsilon_{B,gj}}{\varepsilon_{A,gi} + \varepsilon_{B,gj}},
\]

(31)

where \(\ell_i + \ell_j + 1 = n\) and \(\varepsilon_{A,gi}\) is the excitation energy from state \(g\) to state \(i\) for atom \(A\). The sum implicitly includes the continuum, and \(f_{A,gi}^{(\ell_i)}\) is the oscillator strength of multipole \(\ell_i\) connecting the state \(g\) to the excited state \(i\) for atom \(A\). Considerations of molecular symmetry do not have a direct effect on Eq. (31) when both atoms are in spherically symmetric states.

It is surprising that there has not yet been any calculation of the hydrogen dimer dispersion coefficients based on oscillator strengths from the Dirac equation. This is rectified in Table VIII where the \(C_6\), \(C_8\), and \(C_{10}\) coefficients are given for two hydrogen atoms in their ground states. Table VIII also gives the dispersion coefficients between a hydrogen atom and a He\(^+\) ion.

The use of the Dirac equation leads to the H-H \(C_6\) being reduced by 0.00063 a.u. or 0.0098%. The relative difference is about twice as large as the difference between the rela-
tivistic and non-relativistic polarizabilities. The reduction in the size of $C_6$ is larger for the H-He$^+$ system, being about 0.026%.

V. CONCLUSIONS

A computational investigation based on B-spline methods has been used to investigate the polarizabilities and related sum rules of the hydrogen isoelectronic series. Dipole polarizabilities have been computed to a higher precision than any previous calculations. One distinction with previous calculations is that results were also reported for calculations where the negative-energy Dirac sea is excluded from the intermediate sum. The agreement with previously derived analytic expressions [7, 9, 10] for the dipole polarizability could not be better. High precision calculations of the multipole polarizabilities for $\ell = 2, 3, 4$ are also given. The present results provided a computational validation of the earlier works of Kaneko [7] and Zon [9]. The $\alpha_{\pm}^\ell$ polarizabilities are in agreement with the Kaneko expressions at the $O(\alpha^2 Z^2)$ level. The $\alpha_1^\ell$ polarizability is also in agreement with the expressions of Zon [9], which includes terms at the $O(\alpha^4 Z^4)$ level.

Precise values for other oscillator strength sum rules have also been computed. The sum-rule $S_{\ell}^\pm(0) = \sum_i f_{gi}^{(\ell)} = 0$ provides a valuable check of the numerical reliability of the calculations. The sum-rule, $S_{\ell}^+(0)$ has been shown to be compatible with the $O(\alpha^2 Z^2)$ expression of Levinger et al [35]. It is also compatible with earlier numerical calculations [12, 36].

One aspect of the present work that represents a departure from earlier work has been the treatment of the states of the negative energy sea. Existing practice is that calculations of polarizabilities include the states of the negative energy sea, while calculations of the Bethe sum rule tend to omit these state. The philosophy of the present work has simply been to do two calculations for most properties, those that include the states of the Dirac Sea and those that omit them.

Analytic expressions for $\alpha_{\pm}^\ell$ and $\alpha_1^\ell$ to relative precisions not exceeding $10^{-6}$ have been obtained by fitting an $(\alpha Z)^n$ expansion to the computed polarizabilities. The $C_6$, $C_8$ and $C_{10}$ dispersion coefficients for the long-range H-H and H-He$^+$ interactions were also computed.

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