The theory of quantum electrodynamics, when applied to the hydrogen atom and combined with accurate measurements \cite{1, 2}, leads to the most accurately determined physical constants today \cite{3} and to accurate predictions for transition frequencies. Of crucial importance are higher-order corrections to the bound-state energies, which involve both purely relativistic atomic-physics effects and are mixed with the quantum electrodynamical (QED) corrections. In general, this leads to a double expansion for the energy shifts, both in terms of the QED coupling \( \alpha \) (the fine-structure constant) and the nuclear charge number \( Z \).

As is well known, the leading one-electron energy shifts (due to self-energy and vacuum polarization) in hydrogenlike systems are of order \( \alpha (Z \alpha)^4 \) in units of the electron mass. Analytic calculations for higher excited states in the order \( \alpha (Z \alpha)^6 \) are extremely demanding. For non-\( S \) states, the \( \alpha (Z \alpha)^6 \) corrections have been obtained recently \cite{4}. However, excited \( S \) states are very important for spectroscopy, and the corresponding gap in our knowledge is filled in the current Letter (see Table I). Regarding the two-loop correction, complete results for the \( \alpha^2 (Z \alpha)^5 \) effect were obtained in 1970 (see Ref. \cite{5}). Here, we derive general expressions which allow the determination of the entire two-loop \( \alpha^2 (Z \alpha)^5 \) correction, for all non-\( S \) hydrogenic states and the normalized difference \( \Delta_n \equiv n^3 \Delta E(nS) - \Delta E(1S), \) including the nonlogarithmic term. Together with other available analytic \cite{6, 7} and numerical calculations for the \( 1S \) state \cite{8}, our results allow for a much improved understanding of the higher-order two-loop corrections for a general excited hydrogenic states, and pave the way for an improved determination of fundamental constants from hydrogen spectroscopy.

The one-loop bound-state self-energy, for the states under investigation here, can be written as

\[
\delta^1 E = \frac{\alpha (Z \alpha)^4}{\pi n^3} \left( A_{40} + (Z \alpha)^2 \left[ A_{61} \ln[(Z \alpha)^{-2}] + A_{60} \right] \right),
\]

where the indices of the coefficients indicate the power of \( Z \alpha \) and the power of the logarithm, respectively. We work in a 4-dimensional spacetime with dimension of space is \( d = 3 - \epsilon \). Units are chosen so that \( \hbar = c = e_0 = 1 \), and the electron mass is unit. A nonrelativistic, “Bethe-style” \cite{9} calculation of the contribution due to ultrasoft photons, in the dipole approximation, leads to a dimensionally regularized energy shift \( E_{L0} \),

\[
E_{L0} = -\frac{4 \alpha}{3 \pi} \frac{(Z \alpha)^4}{n^3} \ln k_0 + Z \alpha^2 \left\{ \frac{2}{3 \epsilon} + \frac{10}{9} + \frac{4}{3} \ln[(Z \alpha)^{-2}] \right\} \langle \delta^4(r) \rangle,
\]

where \( \ln k_0 = \frac{n^3}{2(Z \alpha)^3} \langle p^i (H - E) \ln [2|H - E|/(Z \alpha)^2] p^j \rangle \) is the Bethe logarithm, and \( \delta^4(r) = \nabla^2 V/(4\pi) \) is a \( d \)-dimensional Dirac delta function obtained via the action of the Laplacian on the \( d \)-dimensional Coulomb potential \( V(r) = -Z \alpha r^{2-d} / [\Gamma(\frac{d}{2} - 1) \pi^{1-d/2}] \). All matrix elements \( \langle \cdot \rangle \) are to be evaluated with regard to the reference state, as given by a nonrelativistic (Schrödinger–Pauli) wave function, and the summation convention is used throughout this Letter.

### Table I: Values of the nonlogarithmic self-energy correction \( A_{60} \) (“relativistic Bethe logarithm”) for higher excited \( S \) states.

| \( n \) | \( A_{60}(nS) \) | \( A_{60}(1S) \) |
|---|---|---|
| 1 | -30.924 149 46(1) | -31.455 393(1) |
| 2 | -31.840 465 09(1) | -31.914 130(1) |
| 3 | -31.702 501(1) | -31.375 224(1) |
| 4 | -31.564 922(1) | -31.264 257(1) |

Following \cite{4, 10, 11}, we now consider corrections due to the relativistic Hamiltonian, the quadrupole term and the relativistic and retardation corrections to the current. The relativistic correction to the Hamiltonian is

\[
H_R = -\frac{\beta^4}{8} + \frac{\pi}{2} Z \alpha \delta^4(r) + \frac{1}{4} \sigma^{ij} \nabla^i V p^j.
\]

Here, \( \sigma^{ij} \equiv \frac{1}{2i} [\sigma^i, \sigma^j] \). The resulting, dimensionally regularized, correction to the Bethe logarithm is

\[
E_{L1} = \frac{\alpha (Z \alpha)^6}{\pi n^3} \beta_1 + \frac{\alpha}{3 \pi} \left\{ \frac{1}{2 \epsilon} + \frac{5}{6} + L(Z \alpha) \right\} \times \left\{ \frac{1}{8} \nabla^4 V + \frac{1}{4} \sigma^{ij} p^i \nabla^2 V p^j + 2H_R \nabla \sigma^2 V \right\},
\]
where $L(Z\alpha) \equiv \ln \left[ \frac{1}{2}(Z\alpha)^{-2} \right]$, and the Bethe logarithm $\beta_1$ is a generalized Bethe logarithm.

\[
\frac{(Z\alpha)^6}{n^3}\beta_1 = -\frac{4}{3} \sum_{m,n} \frac{(\phi^a)^2 (n_H m_H | m_p | p^a)}{E_m - E_n} \left( E_m - E_n \right) - \frac{2}{3} \langle H_R \rangle \left( \langle H - E \rangle \right) \left( \langle \nabla^2 V \rangle \right) p^a.
\]

We temporarily restore the reference state $\phi$ in the notation of the matrix element, and the sums over $n$ and $m$ include both the discrete as well as the continuous part of the spectrum. The argument of the logarithm in $\beta_1$ is $\ln |(H - E)/(Z\alpha)^2|$, not $\ln |(H - E)/(Z\alpha)^2|$, as in $k_0$, and this fact is important for the precise definition of $\beta_1$, and of all other generalized Bethe logarithms in the following.

In the dimensional scheme, the quadrupole correction $E_{1Lz}$, which was denoted as $F_{1q}$ in former work [10, 11], is found to be expressible as $E_{1Lz} = D_2 + F_3$, where

\[
D_2 = \frac{\alpha}{\pi} \left[ \frac{2\nabla^2 V}{3} \right] \left[ \frac{1}{6} + \frac{103}{60} + 2L(Z\alpha) \right] + \frac{\nabla^4 V}{40} \left[ \frac{1}{6} + \frac{1}{5} + 2L(Z\alpha) \right] + \frac{\nabla^2 V \bar{p}^2}{6} \left[ \frac{1}{2} + \frac{34}{15} + 2L(Z\alpha) \right],
\]

and $F_2$ contains the generalized Bethe logarithm $\beta_2$.

\[
F_2 = \frac{\alpha(Z\alpha)^6}{\pi n^3} = \frac{\alpha}{\pi} \int d\Omega_\eta \left( \delta^{ij} - n^i n^j \right) \left\{ \left( \bar{p}^i (\bar{n} \cdot \bar{r})^2 (H - E)^2 \right) \ln \left[ \frac{H - E}{(Z\alpha)^2} \right] p^j \right\} - \left( \bar{p}^i (\bar{n} \cdot \bar{r}) (H - E)^2 \right) \ln \left[ \frac{H - E}{(Z\alpha)^2} \right] p^j (\bar{n} \cdot \bar{r}).
\]

Here, $\bar{n}$ is a three-dimensional unit vector, and we integrate over the entire solid angle $\Omega_\eta$. Throughout this Letter, $\nabla^2$ and $\nabla^4$ are understood to exclusively act on the quantity immediately following the operator, i.e. $\langle \nabla^2 V \rangle$.

The correction $E_{Lz}$ to the transition current reads $E_{Lz} = D_3 + F_3$, where $F_3 = \alpha(Z\alpha)^6 \beta_3 / \pi n^3$ contains the generalized Bethe logarithm $\beta_3$, and

\[
D_3 = \frac{\alpha}{\pi} \left[ \frac{2}{3} \delta^j - \frac{10}{9} + \frac{4}{3} L(Z\alpha) \right] \left[ \nabla^2 V \bar{p}^j \right] + \frac{2}{3} \left( \nabla^2 V \right) \bar{p}^j.
\]

Here, $\delta^j = \bar{p}^i \bar{p}^j + \frac{1}{2} \sigma^{ij} \nabla V$, and $\nabla^2 \equiv \partial / \partial r^n$ denotes the derivative with respect to the $i$th Cartesian coordinate. The divergences (in $\varepsilon$) in the corrections to the Bethe logarithm are compensated by high-energy virtual photons, which in non-relativistic QED (NRQED) are given by effective operators. From a generalized Dirac equation (see Chap. 7 of Ref. [12]), one easily obtains the effective one-loop potential

\[
\delta^{(1)} V = \frac{1}{6} \frac{\alpha}{\pi} \nabla^2 V + \frac{\alpha}{4\pi} \sigma^{ij} \nabla^i V \bar{p}^j,
\]

which in leading order gives rise to the correction $\langle \delta^{(1)} V \rangle$. This correction is a contribution to the middle-energy part $E_M$, which originates from from high-energy virtual photons, with electron momenta of order $Z\alpha$. The corrections of relative order $(Z\alpha)^2$ to $\langle \delta^{(1)} V \rangle$ involve relativistic corrections to the wave function and to the operators, and a two-Coulomb-vertex scattering amplitude. The sum is

\[
E_M = \langle \delta^{(1)} V \rangle + \frac{2}{\pi} \langle \delta^{(1)} V \nabla^2 H_R \rangle + \frac{\alpha}{\pi} \left[ \frac{1}{192} - \frac{1}{48\varepsilon} \right] \langle \nabla^2 V \rangle + 2 \langle \sigma^{ij} \nabla^i V \rangle \langle \bar{p}^j \rangle
\]

\[
+ \frac{\alpha}{32\pi} \langle \nabla^2 V \rangle \langle \sigma^{ij} \nabla^i V \rangle \langle \bar{p}^j \rangle
\]

\[
- \frac{\alpha}{\pi} \left[ \frac{11}{240} + \frac{1}{40\varepsilon} \right] \langle \nabla^4 V \rangle + \frac{\alpha}{\pi} \frac{11}{48} - \frac{1}{3\varepsilon} \langle \langle \bar{p}^2 \rangle \nabla^2 V \rangle + \frac{\alpha}{\pi} \langle \nabla^4 V \rangle.
\]

The complete one-loop result $\delta^{(1)} E = E_{L0} + E_{L1} + E_{L2} + E_{L3} + E_M$ reads

\[
\delta^{(1)} E = \frac{\alpha}{\pi} \left( Z\alpha \right) \frac{1}{n^3} \left[ \left( \frac{10}{9} + \frac{4}{3} \ln \left( \frac{(Z\alpha)^2}{\varepsilon} \right) \right) \delta_{ij} - \frac{1}{3} \ln k_0 \right] + \frac{\alpha}{4\pi} \langle \sigma^{ij} \nabla^i V \rangle \langle \bar{p}^j \rangle + \frac{\alpha}{\pi} \left( Z\alpha \right) \frac{1}{n^3} \left( \beta_1 + \beta_2 + \beta_3 \right)
\]

\[
+ \frac{\alpha}{\pi} \left\{ \left[ \frac{779}{14400} + \frac{11}{120} \right] \langle \nabla^2 V \rangle \nabla H_R + \frac{1}{2} \langle \sigma^{ij} \nabla^i V \rangle \langle \bar{p}^j \rangle \nabla H_R \right\} + \left[ \frac{23}{576} + \frac{1}{24} \right] \langle \bar{p}^2 \nabla^2 V \rangle + \left[ \frac{589}{720} + \frac{2}{3} \right] \langle \nabla^2 V \rangle \langle \bar{p}^2 \rangle.
\]
The matrix elements in this result can be evaluated using standard techniques. In terms of the notation of Ref. [4], we have $\mathcal{L} = \sum_{i=1}^{3} \beta_i$. Our general result (7), evaluated for hydrogenic states, reproduces the known logarithmic term $A_{60}$, and is consistent with all formulas reported for the nonlogarithmic term in Eqs. (10) and (12) of Ref. [4]. The evaluation of $\mathcal{L}$ is a demanding numerical calculation, and numerical values for non-$S$ states have been presented in Table I of Ref. [4]. Taking advantage of the result (10) for $1S$ and the validity of Eq. (7) for the $nS$-$1S$ difference, we can now proceed to indicate results for the nonlogarithmic term $A_{60}$ for $nS$ states, an evaluation made possible by our generalized NRQED approach (see Table II).

A generalization of our NRQED approach leads to the following general result for the $\alpha^2 (Z\alpha)^6$-term of the complete two-loop Lamb shift (including all diagrams with closed fermion loops),

$$\delta^{(2)}E = \frac{\alpha^2 (Z\alpha)^6}{\pi^2 n^6} \left\{ B_{62} \ln^2[(Z\alpha)^2] + B_{61} \ln[(Z\alpha)^2] + B_{60} \right\} = \frac{\alpha^2 (Z\alpha)^6}{\pi^2 n^6} \left\{ b_L + \beta_4 + \beta_5 + \left[ \frac{38}{45} + \frac{4}{3} L(Z\alpha) \right] N \right\} $$

The leading $\alpha^2 (Z\alpha)^4$-term, given by the $B_{60}$ coefficient, is well known and therefore not included here (for a review see e.g. Appendix A of Ref. [3]). The above expression is valid for $P$, $D$ states, and for the normalized difference $\Delta_n$ of $S$ states. The quantity $N$ is defined in terms of the notation adopted in Refs. [6,13], and the two-loop Bethe logarithm $b_L$ is defined in Refs. [2,14]. Although $b_L$ has been determined numerically only for $S$ states (see Ref. [14]), it represents a well-defined quantity for all hydrogenic states. The logarithmic sum $\beta_5$ is given by Eq. (4), with the replacement $H_R \to \frac{1}{2} \sigma^{ij} V p_i V p_j$. Finally, we have

$$\frac{(Z\alpha)^6}{n^3} \beta_5 = \frac{1}{2} \left\langle \sigma^{ij} V p_i \ln \left[ \frac{H - E}{(Z\alpha)^2} \right] V p_j \right\rangle. \quad (9)$$

Evaluating the general expression (8) for $P$ states, we confirm that $B_{62}(nP) = \frac{4}{27} \frac{n^2 - 1}{n^2}$. Furthermore, we obtain the results

$$B_{61}(nP_{J/2}) = \frac{4}{3} N(nP) + \frac{n^2 - 1}{n^2} \left( \frac{166}{405} - \frac{8 \ln 2}{27} \right),$$

$$B_{61}(nP_{3/2}) = \frac{4}{3} N(nP) + \frac{n^2 - 1}{n^2} \left( \frac{31}{405} - \frac{8 \ln 2}{27} \right). \quad (10)$$

Numerical values for $N(nP)$ can be found in Eq. (17) of [13]. Regarding the nonlogarithmic term $B_{60}$, we fully confirm results for the fine-structure difference of $P$ states [15]. A further important conclusion to be drawn from Eq. (8) is that all logarithmic two-loop terms of order $\alpha^2 (Z\alpha)^6$ vanish for states with orbital angular momentum $l \geq 2$.

We have also verified that the two-loop result (8) is consistent with the normalized $S$-state difference $\Delta_n$ for the logarithmic terms $B_{62}$ and $B_{60}$, as derived in Ref. [4] (using a completely different method). Evaluating all matrix elements in Eq. (8), we are now in the position to obtain the $n$-dependence of the nonlogarithmic term, which we write as $B_{60}(nS) - B_{60}(1S) = b_L(nS) - b_L(1S) + A(n)$, where $A(n)$
is the additional contribution beyond the $n$-dependence of the
two-loop Bethe logarithm. The result for $A(n)$ is

$$A(n) = \left( \frac{38}{45} - \frac{4}{3} \ln(2) \right) \left[ N(nS) - N(1S) \right] - \frac{337043}{129600} - \frac{94261}{216000} n + \frac{902609}{1296000 n^2} + \left( \frac{4}{3} - \frac{16}{9} + \frac{4}{9} \right) \ln^2(2)$$

$$+ \left( \frac{76}{45} + \frac{304}{135 n} - \frac{76}{135 n^2} \right) \ln(2) + \left( \frac{-53}{15} + \frac{35}{2} - \frac{419}{30} n^2 \right) \ln(2) \zeta(2)$$

$$+ \left( \frac{53}{60} - \frac{35}{8} \ln(2) \right) \zeta(3) + \left( \frac{37793}{10800} + \frac{16}{9} \ln^2(2) - \frac{304}{135} \ln(2) + 8 \zeta(2) \ln(2) - \frac{13}{3} \zeta(2) - 2 \zeta(3) \right) [\gamma + \Psi(n) - \ln(n)] .$$

Numerically, $A(n)$ is found to be much smaller than $b_L(nS) - b_L(1S)$, which implies that the main contribution to $B_{00}(nS) - B_{00}(1S)$ is exclusively due to the two-loop Bethe logarithm. As an example, we consider $A(5) = 0.370 042$ and $B_{00}(5S) - B_{00}(1S) = 21.2(1.1)$, where the error is due to the numerical uncertainty of the two-loop Bethe logarithm $b_L(5S)$ (see Ref. [14]).

| $n$ | $\Delta_n$ | $\Delta_{nS}$ | $\Delta_{n1S}$ |
|-----|-------------|-------------|---------------|
| 2   | 187225.70(5) | 12         | 279985.60(10) |
| 3   | 235070.90(7) | 13         | 280529.77(10) |
| 4   | 254419.32(8) | 14         | 280962.77(10) |
| 5   | 264154.03(9) | 15         | 281314.61(11) |
| 6   | 269738.49(9) | 16         | 281604.34(11) |
| 7   | 273237.83(9) | 17         | 281845.77(11) |
| 8   | 275574.90(10)| 18         | 282049.05(11) |
| 9   | 277212.89(10)| 19         | 282221.81(11) |
| 10  | 278405.21(10)| 20         | 282369.85(11) |
| 11  | 279300.01(10)| 21         | 282497.67(11) |

The test of standard model theories and the determination of fundamental constants (specifically, of the Rydberg constant and of the electron mass) provide the main motivations for carrying out the QED calculations in ever higher orders of approximation. Recently, our knowledge of the ground-state Lamb shift has been improved by a fully numerical calculation of the two-loop self-energy [15]. However, because of the structure of the hydrogen spectrum, the decisive quantity for the determination of the Rydberg constant from spectroscopic data is the normalized difference $\Delta_n$ of the $nS - 1S$ Lamb-shift. Elucidating discussions regarding the latter point can be found near Eqs. (2) and (3) of Ref. [16], and in Appendix A of Ref. [17]. Accurate theoretical values for $\Delta_n$ can be inferred from the results reported here and are compiled in Table V of [3]. Using the improved theory as presented in this Letter, it will become possible to determine the Rydberg constant to an accuracy on the level of $10^{-14}$, provided the ongoing experiments concerning the hydrogen $1S - 3S$ transition [17, 18] reach a sub-kHz level of accuracy.

The authors acknowledge helpful conversations with P. J. Mohr and R. Bonciani. This work was supported by EU grant No. HPRF-CT-2001-50034. A.C. acknowledges support by the Natural Sciences and Engineering Research Council of Canada. U.D.J. acknowledges support from the Deutsche Forschungsgemeinschaft (Heisenberg program).

[1] M. Fischer et al., Phys. Rev. Lett. 92, 230802 (2004).
[2] B. de Beauvoir et al., Phys. Rev. Lett. 78, 440 (1997).
[3] P. J. Mohr and B. N. Taylor, Rev. Mod. Phys. 77, 1 (2005).
[4] U. D. Jentschura, E.-O. Le Bigot, P. J. Mohr, P. Indelicato, and G. Soff, Phys. Rev. Lett. 90, 163001 (2003).
[5] T. Appelquist and S. J. Brodsky, Phys. Rev. Lett. 24, 562 (1970) and Phys. Rev. A 2, 2293 (1970); R. Barbieri, J. A. Mignaco and E. Remiddi, Lett. Nuovo Cim. 3, 588 (1970); B. E. Lautrup, A. Peterman and E. de Rafael, Phys. Rev. Lett. B 31, 577 (2000).
[6] K. Pachucki, Phys. Rev. A 63, 042503 (2001).
[7] K. Pachucki and U. D. Jentschura, Phys. Rev. Lett. 91, 113005 (2003).
[8] E. A. Yerokhin, P. Indelicato, and V. M. Shabaev, Phys. Rev. A 71, 040101 (2005).
[9] H. A. Bethe, Phys. Rev. 72, 339 (1947).
[10] K. Pachucki, Ann. Phys. (N.Y.) 226, 1 (1993).
[11] U. Jentschura and K. Pachucki, Phys. Rev. A 54, 1853 (1996).
[12] C. Itzykson and J. B. Zuber, Quantum Field Theory (McGraw-Hill, New York, NY, 1980).
[13] U. D. Jentschura, J. Phys. A 36, L229 (2003).
[14] U. D. Jentschura, Phys. Rev. A 70, 052108 (2004).
[15] U. D. Jentschura and K. Pachucki, J. Phys. A 35, 1927 (2002).
[16] Th. Udem, A. Huber, B. Gross, J. Reichert, M. Prevedelli, M. Weitz, and T. W. H¨ ansch, Phys. Rev. Lett. 79, 2646 (1997).
[17] Th. Udem, private communication (2005).
[18] O. Arnould, private communication (2004).