[1] H. Bethe, Ann. Physik 5, 325 (1930).

[2] H. Bethe, in *Handbuch der Physik*, edited by H. Geiger and K. Sheel (Springer, Berlin, 1933), Vol. 24/1, p. 273.

[3] W. Miller and R. Platzman, Proc. Phys. Soc. (London) A70, 299 (1957).

[4] E. Lassettre and E. White, Ohio State University Research Foundation Scientific Report No. 12 (AFCRC-58-TN-406), 1958 (unpublished).

[5] F. Read and G. Whiterod, Proc. Phys. Soc. (London) 85, 71 (1965).

[6] J. Karle, J. Chem. Phys. 35, 963 (1961).

[7] R. Bonham, J. Phys. Soc. Japan Suppl. 17, 10 (1962).

[8] Y.-K. Kim, M. Inokuti, G. Chamberlain, and S. Mielczarek, Phys. Rev. Letters 21, 1146 (1968).

[9] I. Shimamura, J. Phys. Soc. Japan (to be published).

[10] K. Miller, S. Mielczarek, and M. Krauss, J. Chem. Phys. 51, 26 (1969).

[11] K. Miller, J. Chem. Phys. 51, 5235 (1961).

[12] M. Krauss and S. Mielczarek, J. Chem. Phys. 51, 5241 (1969).

[13] A. Skerbele and E. Lassetre, J. Chem. Phys. 52, 2708 (1970).

[14] S. T. Manson and J. W. Cooper, Phys. Rev. 165, 126 (1968).

[15] J. W. Cooper, Phys. Rev. 128, 681 (1962).

[16] J. W. Cooper, Phys. Rev. Letters 13, 762 (1964).

[17] U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 411 (1968).

[18] S. T. Manson, Bull. Am. Phys. Soc. 14, 485 (1969).

[19] S. T. Manson, *VI ICPEAC Abstracts of Papers* (MIT Press, Cambridge, Mass., 1969), p. 626.

[20] We use this terminology, as suggested by Y. Kim, rather than "Hartree-Fock-Slater" to emphasize that these wave functions are better than Hartree but not quite as good as Hartree-Fock, rather than an improvement on Hartree-Fock as implied by the "Hartree-Fock-Slater" terminology.

[21] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[22] E. McGuire, Phys. Rev. 175, 20 (1968).

[23] M. Ya. Amusia, N. A. Cheredkov, and S. I. Sheftel, Zh. Eksperim. i Teor. Fiz. 58, 618 (1970)[Soviet Phys. JETP 31, 332 (1970)].

[24] M. Ya Amusia and S. I. Sheftel, Ioffe Physico-Technical Institute Report No. 261, 1970 (unpublished).

[25] V. Afrosimov, Yu. Gordeev, V. Lavorov, and S. Shchemelinin, Zh. Eksperim. i Teor. Fiz. 55, 1569 (1968)[Soviet Phys. JETP 28, 82 (1969)].

[26] M. Inokuti, Y.-K. Kim, and R. L. Platzman, Phys. Rev. 164, 55 (1967).

PHYSICAL REVIEW A VOLUME 3, NUMBER 4 APRIL 1971

Lamb Shift and Binding Energies of *K* Electrons in Heavy Atoms[*][†]

A. M. Desiderio and W. R. Johnson
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

(Received 15 April 1970; revised manuscript received 23 September 1970)

The self-energy of K electrons in atoms with atomic numbers in the range $70 \leq Z \leq 90$ is determined numerically. Detailed theoretical evaluations of K-electron binding energies including all effects of $O(\alpha mc^2)$ are given for the four heavy closed-subshell atoms – W, Hg, Pb, and Rn – in the range considered. With the present values of the electron self-energy, the theoretical K-shell binding energies for these elements are found to agree with experimental determinations to better than 1 part in 10^4.

I. INTRODUCTION

Since the appearance of the first Dirac-Hartree-Fock (DHF) calculations of atomic energy levels for heavy atoms,[1] various attempts have been made to understand quantitatively the discrepancies between theoretically determined eigenvalues[2-5] for inner electrons and experimentally determined inner-electron binding energies. A great impetus has been added to this work over the last few years because of the highly accurate analysis of electron binding energies by Bearden and Burr[6] based on precise electron spectroscopy[7] (ESCA) measurements.

It is the purpose of the present paper to analyze the electromagnetic effects of lowest order in the fine-structure constant α, in an attempt to bring the theoretical and experimental understandings of these inner-electron binding energies into closer agreement. The (somewhat surprising) result of our study is that, considering only lowest-order electromagnetic corrections to the K-shell binding energies, we are able to reduce the discrepancy between theoretical and experimental values to less than 0.4 Ry (1 part in 10^4) for each of four closed-subshell atoms – W, Hg, Pb, and Rn – in the range of atomic numbers considered ($Z = 70-90$).

For these heavy atoms the principal electromagnetic effect on inner-electron binding is certainly the nuclear Coulomb field. The Coulomb binding energies are appreciably modified by electrostatic screening; these screening effects are accurately described for heavy closed-shell atoms by DHF calculations. We take as a basis for the discussion of electromagnetic effects the bound-interaction representation of quantum electrodynamics,[8] in which it is assumed that the electron-positron field satis-

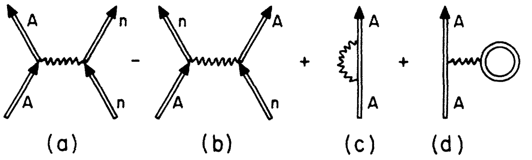

FIG. 1. Lowest-order corrections to electron binding energies. (a) and (b) represent the retarded Breit interaction; (c) and (d) represent the electron self-energy and vacuum-polarization parts of the Lamb shift for electron *A*. The electrostatic contributions to (a) and (b) are to be omitted from the perturbation, and the interactions are to be summed over occupied orbitals *n* to give the energy shift of electron *A*.

fies the Dirac equation in a predetermined DHF potential. That is, we apply the usual Feynman rules to compute the energy shifts, but consider the *electrostatic electron-electron interaction* together with the nuclear Coulomb field to be included in a self-consistent potential $V(r)$, which governs the noninteracting fields. To lowest order in the fine-structure constant, the corrections to the orbital energy of an electron A (i.e., to the DHF eigenvalue of A) are represented by the diagrams of Fig. 1.

Figures 1(a) and 1(b) represent direct and exchange interactions between the electron under consideration (A) and another electron in an occupied orbital (n). It is, of course, understood that the unretarded charge-charge interactions represented in Figs. 1(a) and 1(b) are to be excluded from the perturbation [since they are already included in the self-consistent potential $V(r)$] and that the perturbation is to be summed over all occupied orbitals n. An elegant derivation of the interaction resulting from Figs. 1(a) and 1(b) is given by Bethe and Salpeter.[9] The energy shift represented by Figs. 1(a) and 1(b) is composed of two distinct parts: The larger effect is the magnetic energy shift which results from the current-current interaction and the remaining part is the retardation correction to the charge-charge interaction. We expand the magnetic and retardation corrections in powers of αZ and retain only the lowest-order contributions (a procedure which is justified to within several percent for elements in the range $Z = 70-90$). The resulting interaction is then identical to the Breit interaction.[10] To compute the magnetic and retardation energies we reduce the Breit interaction to Slater radial integrals using techniques which are equivalent to, but somewhat simpler than, the methods discussed previously in the literature by Grant[2] and by Kim.[11]

Figure 1(c) represents the electron self-energy. For a $1s_{1/2}$ state in hydrogen this represents a small fraction (3×10^{-7}) of the electron binding. Since the electrostatic energy grows as Z^2 while the self-energy grows as Z^4, the self-energy represents a sizable fraction ($\sim 2\times10^{-3}$) of the binding in heavy atoms. For light atoms, the Bethe formula[12] allows an accurate determination of the electron self-energy. For heavier one-electron atoms, the generalization of the Bethe formula developed by Erickson and Yennie,[13] giving corrections up to order $\alpha(\alpha Z)^6 mc^2$, would appear to provide a useful representation of the self-energy. One finds, however, that the various terms in the αZ expansion in the $Z = 70-90$ range are all of the same order of magnitude and that the corresponding determination of the self-energy is inaccurate due to the poor convergence of the perturbation series.

As an alternative to the series expansion we adopt the method developed by Brown, Langer, and Schaefer[14] to study the self-energy in heavy atoms. These authors use an angular momentum decomposition of the electron propagator to reduce the self-energy to a form amenable to numerical evaluation. Application of the technique to K electrons in Hg ($Z = 80$) has been given by Brown and Mayers,[15] who obtain an energy shift $\Delta E = 41$ Ry with an estimated error of 2 to 3 Ry. We have reexamined the Brown-Mayers calculation for an electron in the Coulomb field of a Hg nucleus and find a value $\Delta E = 15.0$ Ry or about one-third of the previous result. In Sec. II we outline the self-energy calculation and make detailed comparisons between our values and the corresponding values of Brown and Mayers. For our later applications to one-electron binding energies in heavy atoms, we generalize the previous technique slightly to include electrostatic screening effects in the unperturbed states.

Figure 1(d) represents the energy shift due to vacuum polarization. For the case of an electron in a nuclear Coulomb field, the vacuum polarization has been studied to all orders in αZ by Wichmann and Kroll,[16] who establish that to within several percent the vacuum-polarization shift can be represented as the expectation of the Uehling potential. In Sec. III we present numerical results determined from the Coulomb field Uehling potential[17] and discuss the question of electron screening corrections to the corresponding energy shifts.

In addition to the effects considered above, there are two other important corrections of order α to be considered. The first of these corrections is rearrangement. In comparing the binding energy with experiment, it is necessary to compute the total energy difference between the atom and the inner-electron ion after rearrangement. If there were no effects of charge redistribution on the one-electron orbitals after ionization, then, according to Koopmans's theorem,[18] the atom-ion energy difference would equal the DHF eigenvalue of the ionized electron. The small difference between the atom-ion energy and the DHF eigenvalue due to charge redistribution is called the rearrangement energy.

The second effect of order α not included in Fig. 1 is the departure of the nuclear potential from a Coulomb potential at small distances. We treat this nuclear finite-size effect by replacing the nuclear Coulomb field by the field of a spherically symmetric charge distribution with a Fermi shape

$$\rho(r) \propto 1/[e^{(r-c)/a}+1] ,$$

where c is the half-density radius determined from electron scattering experiments,[19] and $t = 2 \ln 9a$ is the 90–10% fallout distance. The values of $c = 1.07A^{1/3}\times 10^{-13}$ cm and $t = 2.4\times 10^{-13}$ cm were used, where A is the atomic weight of the nucleus.

Second- and higher-order corrections to the electrostatic DHF energy of the atom are termed correlation effects. There are several methods of estimating correlation effects in atoms, all leading to energy shifts in the K-electron binding of about -0.1 Ry. A summary of various studies of correlation effects in atoms is given by Cowan.[20] While we recognize the speculative nature of the precise value of the correlation energy deduced from the empirical analysis of Ref. 20, we nevertheless include this particular higher-order effect with our first-order calculations to illustrate its sign and order of magnitude. Omitting correlation entirely from the theoretical effects considered worsens the agreement with experiment from 0.4 Ry to 0.5 Ry for the examples considered. It must be emphasized that there are other effects of order α^2 which we have not included, such as the higher-order corrections to the self-energy and vacuum polarization, as well as polarization effects resulting from symmetry breaking in the ion which would give direct contributions to the magnetic energy in the ion.[21]

As an indication of the relative sizes of the effects discussed above, we list, in order of decreasing importance with respect to a K electron in Hg, approximate values of the various contributions: (a) electrostatic energy ~ -6000 Ry, (b) magnetic energy $\sim +25$ Ry, (c) electromagnetic self-energy $\sim +15$ Ry, (d) rearrangement energy ~ -7 Ry, (e) nuclear finite-size effect $\sim +4$ Ry, (f) vacuum-polarization energy ~ -3 Ry, (g) electric retardation energy ~ -2 Ry, and (h) correlation effects ~ -0.1 Ry.

Detailed values of the above effects are given for K electrons in the closed-subshell atoms W, Hg, Pb, and Rn, together with a comparison with experimental energy levels in Sec. III.

II. SELF-ENERGY

In this section we generalize the work of Brown, Langer, and Schaefer[14] to include electrons in excited states in a non-Coulomb, but spherically symmetric, potential. Below we compare the various terms of the self-energy calculated by Brown and Mayers[15] for the case of a K electron in the Coulomb field of Hg nucleus with our results, and give numerical values for the self-energy of K electrons in a pure Coulomb field as well as a screened Coulomb field for atoms with atomic numbers in the range $Z = 70-90$.

A. Formulation

To clarify our notation and conventions we write down the Dirac equation for an electron in a time-independent external field,

$$H_0 u_n(\vec{x}) = E u_n(\vec{x}), \tag{1}$$

where

$$H_0 = -i\vec{\alpha}\cdot\vec{\nabla} + \beta m + V(x),$$

$\vec{\alpha}$ and β are the convential Dirac matrices, and $V(x)$ is the potential energy. Natural units ($\hbar = c = 1$, unit of length $= 1$ cm) are used throughout. For an electron in a pure Coulomb field, $V(x) = -\alpha Z/|\vec{x}|$, where $\alpha = e^2/4\pi \simeq \frac{1}{137}$ (the fine-structure constant). Since H_0 commutes with J^2, the total angular momentum, and with J_z its projection, we are able to classify solutions of Eq. (1) according to angular momentum, and can write $u(\vec{x})$ in the form

$$u(\vec{x}) = \frac{1}{x}\begin{pmatrix} iG_\kappa(x, E_n)\Omega_{\kappa m}(\hat{x}) \\ F_\kappa(x, E_n)\Omega_{-\kappa m}(\hat{x}) \end{pmatrix}. \tag{2}$$

The radial functions G_κ and F_κ are the large and small components, respectively, of the Dirac wave function. The quantities $\Omega_{\kappa m}(\hat{x})$ are spherical spinors[22] which are eigenfunctions of J^2, J_z, the orbital angular momentum L^2, and the electron spin S^2. They can be expressed as

$$\Omega_{\kappa m}(x) = \sum_{\lambda} C(l, \tfrac{1}{2}, j; m-\lambda, \lambda) Y_l^{m-\lambda}(\hat{x})\chi_\lambda , \tag{3}$$

where $C(l, \frac{1}{2}, j; m-\lambda, \lambda)$ is a Clebsch-Gordan coefficient, $Y_l^m(\hat{x})$ is a spherical harmonic, and χ_λ is a two-component Pauli spinor. The quantity κ is given by

$$\kappa = \pm(j + \tfrac{1}{2}) \text{ as } l = j \pm \tfrac{1}{2} .$$

If we express H_0 in a spherical basis, Eq. (1) takes the form

$$\begin{aligned} &\left(\frac{d}{dx} + \frac{\kappa}{x}\right) G_\kappa(x, E) + [m + E - V(x)] F_\kappa(x, E) = 0, \\ &\left(\frac{d}{dx} - \frac{\kappa}{x}\right) F_\kappa(x, E) + [m - E + V(x)] G_\kappa(x, E) = 0. \end{aligned} \tag{4}$$

In the numerical calculations presented later, $V(x)$ is chosen as a nuclear Coulomb potential for comparison with the previous calculations of Refs. 14 and 15, and replaced by a Dirac-Hartree-Fock-Slater (DHFS)[1] potential to determine the influence of screening and nuclear size on the self-energy.

The terms contributing to the renormalized self-energy of an electron in an external field as given by Brown *et al.* [see Eq. (28) of Ref. 14] are

$$\Delta E_{\text{self-energy}} = \Delta E_0 - \Delta E_x - (1/2\pi i)\,(X_B + X_C - Y_L)\ , \tag{5}$$

where $\Delta E_0 - \Delta E_x$ is the difference between the self-energy graph of Fig. 1(c) and the same graph with a free-electron propagator in the intermediate state; X_B and X_C are the charge renormalization and finite parts, respectively, of ΔE_x; and Y_L is a spurious term which results from performing the evaluation of $\Delta E_0 - \Delta E_x$ noncovariantly. In our notation the last part of Eq. (5) is given by

$$-(1/2\pi i)(X_B + X_C - Y_L) = \Delta E^{(2)} + \Delta E_c\ , \tag{6}$$

where

$$\Delta E^{(2)} = -\frac{5\alpha}{4\pi}\langle V(x)\rangle_A - 2\pi^2\alpha\int d^3p\,\bar{u}_A(\vec{\mathrm{p}}) \times \frac{\xi}{1-\xi}\left[m\left(1-\frac{2-3\xi}{1-\xi}\ln\xi\right) - (m + i\gamma_\mu p_\mu)\left(1+\frac{2-\xi}{1-\xi}\ln\xi\right)\right]u_A(\vec{\mathrm{p}}), \tag{7}$$

$$\Delta E_c = -\frac{\alpha}{2\pi}\langle V(x)\rangle_A\int_0^\infty \frac{d\omega}{(\omega^2+m^2)^{1/2}}\ , \tag{8}$$

and

$$\xi = (\vec{\mathrm{p}}^2 - E_A^2 + m^2)/m^2,\quad p_u = (\vec{\mathrm{p}},\ iE_A)\ ,$$

$$\gamma_\mu = (-i\beta\vec{\alpha},\ \beta),\ \text{and}\ \bar{u}_A = u_A^\dagger\beta.$$

The quantity $\langle V(x)\rangle_A$ is the expectation of the potential energy over the state of interest A, and $u_A(\vec{\mathrm{p}})$ is the Fourier transform of the wave function of state A, given by

$$u_A(\vec{\mathrm{p}}) = \frac{1}{(2\pi)^3}\int d^3x\, e^{-i\vec{\mathrm{p}}\cdot\vec{\mathrm{x}}}u_A(\vec{\mathrm{x}})\ . \tag{9}$$

Since we will be interested in using numerically determined self-consistent field wave functions for $u_A(\vec{\mathrm{x}})$, it is necessary to reduce $\Delta E^{(2)}$ to a form convenient for numerical evaluation. Using Eqs. (2) and (9), and expanding $e^{-i\vec{\mathrm{p}}\cdot\vec{\mathrm{x}}}$ in terms of spherical harmonics it can be shown that

$$\Delta E^{(2)} = -\frac{5\alpha}{4\pi}\langle V(x)\rangle_A - \frac{2\alpha}{\pi^2}\int Q^-(p)\frac{\xi\ln\xi}{\xi-1}p^2dp + \frac{\alpha}{\pi^2}\frac{\kappa_A}{|\kappa_A|}\int G_{\kappa_A}(p)F_{\kappa_A}(p)Z(\xi)p^3dp + \frac{\alpha E_A}{2\pi^2}\int Q^+(p)Z(\xi)p^2dp, \tag{10}$$

where

$$Q^\pm(p) = G_{\kappa_A}^2(p) \pm F_{\kappa_A}^2(p),$$

$$G_{\kappa_A}(p) = \int G_{\kappa_A}(x)j_{l_A}(px)x\,dx,$$

$$F_{\kappa_A}(p) = \int F_{\kappa_A}(x)j_{\bar{l}_A}(px)x\,dx,$$

$$Z(\xi) = \frac{\xi}{\xi-1}\left(1+\frac{\xi-2}{\xi-1}\ln\xi\right)\ .$$

The quantity l_A is the orbital quantum number of state A, and $\bar{l}_A = 2j_A - l_A$, where j_A is the total angular momentum quantum number of A. The spherical Bessel function is denoted by $j_l(px)$.

Evaluation of ΔE_0 was carried out using the same general technique as Brown *et al.*[14] Specifically, the intermediate-state electron propagator was expanded in terms of angular momentum solutions of the Dirac equation; integration over angles associated with the photon momentum $\vec{\mathrm{k}}$ was performed followed by integration over $d\,|\vec{\mathrm{k}}\,|$, leaving an integral over the photon energy ω to be carried out numerically. Integration over angles was facilitated by expanding $u_A^\dagger(\vec{\mathrm{x}})\,\vec{\alpha}\,u_B(\vec{\mathrm{x}})$ in terms of spherical vector harmonics which are discussed, for example, by Akhiezer and Berestetskii.[23]

The ω integration was reduced to a form convenient for numerical purposes by rotating the integration path from the real to the imaginary ω axis. Generally, pole terms appear when the integration is transformed from the real ω axis to the imaginary axis in the complex ω plane. These pole terms arise from intermediate-state transitions to states more tightly bound than the state of interest. We find that the general result for ΔE_0 can be expressed as

$$\Delta E_0 = -\frac{\alpha}{2\pi^2}\int_0^\infty \omega\,d\omega\int_0^\infty dr\int_0^r dx\,\mathrm{Re}\left(\sum_\kappa \frac{S_\kappa(x,r,i\omega)}{\Delta_\kappa(E_A - i\omega)}\right) + i\pi R_0 + 2\pi i R_N, \tag{11}$$

where

$$S_\kappa(x,r,\omega) = 4\pi(2j+1)\sum_{J=0}^{\infty}\left\{(2J+1)\Lambda_{-\kappa J\kappa_A}\frac{(\kappa_A+\kappa)^2}{J(J+1)}B_J Q^{\infty+}(r)Q^{0+}(x)\right.$$

$$+(2J+1)\Lambda_{\kappa J\kappa_A}\left[\frac{J}{2J+1}B_{J-1}\left(Q^{\infty -}(r)+\frac{\kappa-\kappa_A}{J}\,Q^{\infty +}(r)\right)\left(Q^{0-}(x)+\frac{\kappa-\kappa_A}{J}\,Q^{0+}(x)\right)\right.$$

$$\left.+\frac{J+1}{2J+1}B_{J+1}\left(Q^{\infty -}(r)+\frac{\kappa_A-\kappa}{J+1}\,Q^{\infty +}(r)\right)\left(Q^{0-}(x)+\frac{\kappa_A-\kappa}{J+1}\,Q^{0+}(x)\right)-B_J\,P^{\infty}(r)P^{0}(x)\right]\Bigg\}\ , \qquad (12)$$

$$Q^{\infty,0\pm}(x)=G_{\kappa_A}(x,E_A)F_{\kappa}^{\infty,0}(x,E_A-\omega)$$

$$\pm F_{\kappa_A}(x,E_A)G_{\kappa}^{\infty,0}(x,E_A-\omega),$$

$$P^{\infty,0}(x)\ =G_{\kappa_A}(x,E_A)G_{\kappa}^{\infty,0}(x,E_A-\omega)$$

$$+F_{\kappa_A}(x,E_A)F_{\kappa}^{\infty,0}(x,E_A-\omega),$$

$$B_J=h_J^{(1)}(\omega r)j_J(\omega x),$$

$$\Lambda_{\kappa_B k\kappa_A}=\frac{[C(j_B,k,j_A;\tfrac{1}{2},0)]^2}{2j_A+1}\Pi_{l_A k l_B}, \qquad (13)$$

and

$$\Pi_{l_A k l_B}=\begin{cases}1, & l_A+k+l_B=\text{even}\\ 0, & l_A+k+l_B=\text{odd}.\end{cases}$$

The quantities $G_{\kappa}^{\infty,0}(x,E_A-\omega)$ and $F_{\kappa}^{\infty,0}(x,E_A-\omega)$ are solutions of Eq. (4) which are bounded at infinity (zero) but not at zero (infinity) for an energy $E=E_A-\omega$, and $\Delta_{\kappa}(E_A-\omega)$ is the Wronskian of these solutions. The spherical Hankel function of the first kind is represented by $h_J^{(1)}(\omega r)$, and the quantum numbers j, l, κ, and j_A, l_A, κ_A refer to the intermediate state and the state of interest, respectively. It should be noted that $S_{\kappa}(x,r;i\omega)$ in Eq. (11) is defined by Eq. (12) with the replacement $\omega\to i\omega$.

The term $i\pi R_0$ is given by

$$i\pi R_0=-\frac{\alpha}{4\pi}\int_0^{\infty}dr\int_0^{r}dx\,S_{\kappa}(x,r,0)\ ,$$

where $S_{\kappa}(x,r,0)$ is defined by setting ω equal to zero and making the replacement

$$h_J^{(1)}(\omega r)j_J(\omega x)\to\frac{1}{2J+1}\,\frac{x^J}{r^{J+1}}$$

in $S_{\kappa}(x,r,\omega)$ and

$$2\pi iR_N=\frac{\alpha}{2\pi}\sum_n\omega_n\int_0^{\infty}dr\int_0^{r}dx\,\mathrm{Im}S_{\kappa_n}(x,r,\omega_n)\ ,$$

where $\omega_n=E_A-E_n>0$, and the sum over n is over all those subshells more tightly bound than state A.

The term ΔE_x is obtained from $\Delta E_0-i\pi R_0-2\pi iR_N$ with the potential energy set equal to zero for the intermediate-state wave functions but not for the bound-state wave functions describing state A.

For the special case of a $1s_{1/2}$ electron in a pure Coulomb field, our general expression reduces to that given by Brown *et al.*[14] except for a factor of 2 in the term $\Delta E_0-i\pi R_0$. The expression for $\Delta E_0-i\pi R_0$ given in Ref. 14 is clearly in error as one can see by following the calculation from Eqs. (20)–(25).

B. Numerical Details

For the case of a $1s_{1/2}$ electron in the field of a nucleus with $Z=80$, we carried out the numerical evaluation of the self-energy. In Table I we show

TABLE I. Integrand of $-(\Delta E_0-\Delta E_x-i\pi R_0)$ as a function of the angular momentum l and photon energy ω for a $1s_{1/2}$ electron in the pure Coulomb field of a Hg nucleus. Values are given in units of αmc^2 and powers of ten.

$l \backslash \omega$	0.07	0.34	0.77	1.30	1.83	2.26	2.53
0	0.2114 +0	0.7265 -1	0.2162 -1	0.8597 -2	0.4421 -2	0.2826 -2	0.2211 -2
1	0.1985 -1	0.2164 -1	0.1350 -1	0.6616 -2	0.3284 -2	0.1873 -2	0.1331 -2
2	0.1445 -1	0.1366 -1	0.9398 -1	0.5498 -2	0.3250 -2	0.2151 -2	0.1684 -2
3	0.9989 -2	0.9222 -2	0.6842 -1	0.4461 -2	0.2912 -2	0.2078 -2	0.1701 -2
4	0.7009 -2	0.6530 -2	0.5139 -2	0.3615 -2	0.2526 -2	0.1895 -2	0.1597 -2
5	0.5094 -2	0.4811 -2	0.3964 -2	0.2953 -2	0.2172 -2	0.1692 -2	0.1455 -2
6	0.3834 -2	0.3664 -2	0.3128 -2	0.2437 -2	0.1867 -2	0.1498 -2	0.1311 -2
7	0.2975 -2	0.2869 -2	0.2518 -2	0.2035 -2	0.1611 -2	0.1325 -2	0.1175 -2
8	0.2368 -2	0.2299 -2	0.2063 -2	0.1717 -2	0.1397 -2	0.1172 -2	0.1053 -2
9	0.1926 -2	0.1881 -2	0.1716 -2	0.1463 -2	0.1218 -2	0.1041 -2	0.9437 -3
10	0.1596 -2	0.1564 -2	0.1447 -2	0.1259 -2	0.1069 -2	0.9271 -3	0.8479 -3
11	0.1342 -2	0.1319 -2	0.1234 -2	0.1091 -2	0.9433 -3	0.8288 -3	0.7638 -3
12	0.1144 -2	0.1127 -2	0.1064 -2	0.9548 -3	0.8369 -3	0.7438 -3	0.6902 -3
13	0.9860 -3	0.9739 -3	0.9259 -3	0.8408 -3	0.7464 -3	0.6702 -3	0.6255 -3
14	0.8585 -3	0.8493 -3	0.8124 -3	0.7453 -3	0.6690 -3	0.6060 -3	0.5687 -3
15	0.7541 -3	0.7470 -3	0.7182 -3	0.6647 -3	0.6025 -3	0.5502 -3	0.5188 -3
16	0.6677 -3	0.6621 -3	0.6393 -3	0.5962 -3	0.5450 -3	0.5012 -3	0.4746 -3

TABLE II. Final contributions as functions of ω.

ω	$\Delta E_0 - \Delta E_x{}^{a} - i\pi R_0$	Extrapolated[b]	Total integrand	Counter term[c]
0.07	−0.2863 +0	−0.1092 −1	−0.2972 +0	0.6666 −1
0.34	−0.1465 +0	−0.1089 −1	−0.1574 +0	0.6333 −1
0.77	−0.7673 −1	−0.1078 −1	−0.8751 −1	0.5287 −1
1.30	−0.4555 −1	−0.1061 −1	−0.5615 −1	0.4073 −1
1.83	−0.3007 −1	−0.1037 −1	−0.4044 −1	0.3207 −1
2.26	−0.2238 −1	−0.9997 −2	−0.3238 −1	0.2699 −1
2.53	−0.1895 −1	−0.9794 −2	−0.2875 −1	0.2453 −1

[a] Sum of angular momentum terms from Table I.

[b] Extrapolated remainder of angular momentum series.

[c] Counter term ΔE_c from Eq. (8).

the integrand of $\Delta E_0 - \Delta E_x - i\pi R_0$ ($2\pi i R_N$ is zero for a $1s_{1/2}$ electron) as a function of ω and l. For values of κ greater than 16, an extrapolation procedure was employed. Brown and Mayers[15] have shown that the angular momentum terms in Eq. (11) behave as $1/l^2$ in the asymptotic region. To avoid numerical cancellation in the extrapolation and to assure that the extrapolated values behaved as $1/l^2$ for large values of l, the last three evaluated terms ($l = 14, 15, 16$) in the series were inverted and fitted to a parabola. The angular momentum terms in the range $l = 17-100$ were then extrapolated. At $l = 100$ the series was assumed to have taken on a pure $1/l^2$ behavior and the remainder $C\sum_{l=101}^{\infty} 1/l^2$ was added to the sum, where the constant C was determined by $C = (100)^2/A_{100}$ with A_{100} being the extrapolated value for $l = 100$. This procedure was tested on the series

$$\sum_{l=1}^{\infty} \frac{2l^2 + 3l + 1}{l^4},$$

and was found to give the exact answer to an accuracy of better than 1 part in 10^6. As can be seen in Table I, the angular momentum terms diminish as $1/l^2$ for large l and a given value of ω.

The integrand of $\Delta E_0 - \Delta E_x - i\pi R_0$ was evaluated along with the counter term at seven values of ω, and integrated from 0 to 2.6 using a Gauss-Legendre quadrature formula. This formula was chosen because of its great accuracy for a comparatively small number of points. The remaining part of the integral was extrapolated by fitting the *reciprocal* of the last three values of the integrand to form an expression of the form $A\omega^3 + B\omega + C/\omega$. This form was chosen because the difference between the integrand and the counter term behaves as $1/\omega^3$ in the asymptotic region and consists only of odd powers in ω. The values of the integrand from 2.6 to infinity were evaluated using the extrapolated form, and then these values were integrated. This technique was tested on the integral

$$\int_0^{\infty} [(1+\omega^2)^{-1/2} - (2+\omega^2)^{-1/2}]\,d\omega$$

and gave the correct answer to better than 2 parts in 10^5.

In Table II we show the sum of the angular momentum terms given in Table I, the extrapolated values of the remainder of the angular momentum series, the resulting total value of $\Delta E_0 - \Delta E_x - i\pi R_0$, and the values of the counter term in Eq. (8), all as functions of ω. As can be seen, the integrand behaves as $1/\omega$ in the asymptotic region and approaches the negative of the counter term. These requirements had to be met in order for the numerical calculations to be correct.

To check our computer program we ran it for a $1s_{1/2}$ electron in a pure Coulomb field for atoms with atomic numbers in the range $Z = 70-90$. The results obtained were found to behave dominantly as Z^4 and are given in Table III along with the results of Brown and Mayers for $Z = 80$. As is evident, the present value of the self-energy for $Z = 80$ is smaller than the Brown-Mayers value by a factor of approximately 3. The two terms $\Delta E^{(2)}$ and "main term" in Table III which disagree with Ref. 15 have been carefully checked for numerical accuracy.

It is hard to judge the accuracy of our numerical calculations, but changing the upper limit on the ω integration from 2.6 to 2.5 reproduced the same answer to 0.05%. This would then have to be a lower bound on the error in our numerical work.

In Table IV we present values for the "screened"

TABLE III. Various contributions to the self-energy of a K electron in the *Coulomb field* of a heavy nucleus as a function of the nuclear charge Z. Values are in Ry.

Term	$Z=70$	$Z=75$	$Z=80$	$Z=85$	$Z=90$	$Z=80$[a]
$i\pi R_0$	+43.8	+47.1	+50.4	+53.8	+57.4	+50.4
$\Delta E^{(2)}$	− 8.0	− 6.6	− 4.7	− 2.4	+ 0.4	+ 6.9
Main term	−26.7	−28.6	−30.7	−32.3	−34.3	−16.2
Total	+ 9.1	+11.9	+15.0	+19.1	+23.5	+41.1

[a] Previous results of Brown and Mayers, Ref. 15.

TABLE IV. Self-energy and vacuum-polarization energy of a K electron in a *screened* Coulomb field as a function of the nuclear charge Z. Values are in Ry.

Z	Self-Energy	Vacuum polarization[a]	Total Lamb shift[b]
70	+ 8.95	−1.70	+ 7.25
71	+ 9.43[c]	−1.82	+ 7.61
72	+ 9.92[c]	−1.89	+ 8.03
73	+10.44[c]	−2.08	+ 8.36
74	+10.96	−2.23	+ 8.73
75	+11.53	−2.38	+ 9.15
76	+12.10[c]	−2.54	+ 9.56
77	+12.70[c]	−2.71	+ 9.99
78	+13.33[c]	−2.89	+10.44
79	+13.98[c]	−3.08	+10.90
80	+14.65	−3.29	+11.36
81	+15.35	−3.50	+11.85
82	+16.09	−3.74	+12.35
83	+16.85[c]	−3.98	+12.87
84	+17.64[c]	−4.24	+13.40
85	+18.47	−4.52	+13.95
86	+19.33	−4.82	+14.51
87	+20.23[c]	−5.14	+15.09
88	+21.16	−5.47	+15.69
89	+22.13[c]	−5.83	+16.30
90	+23.14	−6.21	+16.93

[a] Screening was accounted for in the vacuum polarization by reducing the Coulomb field value by 2% as explained in the text.

[b] Sum of self-energy and vacuum-polarization energy.

[c] Value obtained by using a Lagrange four-point interpolation formula and the values at the points $Z=75$, 80, 85, 90. Interpolated values were found to agree to better than 0.05% with the calculated values.

self-energy in the range 70–90. Screening and nuclear finite-size effects are included in the self-energy calculation by replacing the Coulomb wave functions and potentials by numerically determined DHFS wave functions and potentials. One finds that throughout the range considered, the effects of screening and nuclear finite size on the electron self-energy can be represented approximately by reducing the Coulomb field value by 2%. Interpolation was carried out for several values in the table because of computer time limitations. Interpolated values were found to agree with several calculated values to an accuracy of better than 0.05%.

III. COMPARISON OF THEORETICAL BINDING ENERGIES WITH EXPERIMENT

In this section we make use of the values of the K-electron self-energy just discussed, and numerical values of the other electromagnetic effects discussed in Sec. I to give theoretical values for K-electron binding energies in four heavy closed-shell atoms – W, Hg, Pb, and Rn. In Table V we list numerical values of the various effects, and compare the resulting theoretical binding energies with experiment. We will now review how each effect listed was determined.

A. Electric Energy

The electric energy was computed using a standard DHF technique in which magnetic and retardation effects were neglected. The electric energy results from the electrostatic Coulomb interaction of the electron with the nucleus and with all the other electrons. The effects of rearrangement are included in the electric energy by computing the total atom-ion electrostatic-energy difference. Since a nuclear model with a Fermi shape was used in the DHF program, the effect of finite nuclear size was automatically included in the electric energy. The DHF values for the electric, magnetic, and retardation energies were communicated to us by Mann of Los Alamos. As a check on the DHF energies, we computed DHFS values for the electric, magnetic, and retardation energies and our values differed very little from those given to us by Mann. The largest difference was in the electric energy of Pb and that amounted to approximately 0.2 Ry. We give Mann's DHF values in Table V because they are, in principle, more accurate than our DHFS energies.

B. Magnetic and Retardation Energy

The Breit operator which contains both magnetic and retardation terms was treated as a first-order perturbation using the DHF wave functions as the unperturbed wave functions of the system. In order to take into account the effect of rearrangement, total magnetic and retardation atom-ion energy differences were computed. The Breit operator is correct up to order $(v/c)^2$. In a forthcoming paper, Mann and one of us (W. R. J.) discuss the technique used to evaluate the magnetic and retardation energy, and calculate higher-order (αZ) corrections to the Breit interaction, which, for heavy atoms considered in this paper, amounts to a shift in the sum of the magnetic and retardation energies of approximately 2%.

C. Self-Energy

The self-energy was evaluated using DHFS wave functions and potentials. It is estimated that the error made in using DHFS wave functions instead of DHF wave functions is much less than the inherent error in the numerical procedures used to evaluate the self-energy.

The effect of rearrangement on the self-energy was neglected. This effect should be exceedingly small because the self-energy is a one-body operator as contrasted with the two-body operator involved in the magnetic and retardation energies and, consequently, a slight change in the K-electron

TABLE V. Comparison of theoretical and experimental binding energies for *K* electrons in heavy $J=0$ atoms in Ry.

Effect considered	W $Z=74$	Hg $Z=80$	Pb $Z=82$	Rn $Z=86$
Electric energy[a]	-5135.99	-6141.65	-6504.80	-7275.37
Magnetic energy[a]	$+\ 18.53$	$+\ 24.09$	$+\ 26.21$	$+\ 30.87$
Self-energy	$+\ 10.96$	$+\ 14.65$	$+\ 16.09$	$+\ 19.33$
Vacuum polarization	$-\ 2.23$	$-\ 3.29$	$-\ 3.74$	$-\ 4.82$
Retardation energy[a]	$-\ 1.39$	$-\ 1.80$	$-\ 1.96$	$-\ 2.30$
Correlation energy[b]	$-\ 0.08$	$-\ 0.08$	$-\ 0.08$	$-\ 0.08$
Theoretical *K* energy	-5110.20	-6108.08	-6468.28	-7232.47
Experimental *K* energy[c]	-5110.46 ± 0.02	-6108.39 ± 0.06	-6468.67 ± 0.05	-7232.73 ± 0.89

[a] J. B. Mann (private communication).

[b] An order-of-magnitude estimate based on the empirical work of R. D. Cowan, Ref. 20.

[c] J. A. Bearden and A. F. Burr, Ref. 6; corrected for photoelectric work function, Ref. 24.

wave function would induce an even smaller change in the self-energy.

D. Vacuum Polarization

The vacuum-polarization energy was computed by evaluating the Uehling[17] potential with Coulomb field wave functions. The effect of screening and finite nuclear size on the vacuum polarization was approximated by reducing the Coulomb field values by 2% – an empirical rule which applied to the self-energy. Since Wichmann and Kroll[16] have established that the dominant contribution, in powers of αZ, to the vacuum polarization is given by the expectation of the Uehling potential, we believe that the vacuum-polarization values are in error by no more than 10%. The resulting screened values for the vacuum polarization are listed in Table III for all elements in the range considered together with the self-energy and total Lamb shift.

E. Correlation Energy

Correlation energy is the correction added to the DHF approximation to account for the error involved in approximating the many-electron state by a product of one-electron states. Correlation energy was taken to be -0.08 Ry/electron from the semiempirical analysis of Cowan.[20] The effect of rearrangement on the correlation energy is expected to be negligible.

F. Modification of Experimental Energies

The experimental binding energies were taken from a table of electron binding energies by Bearden and Burr.[6] We corrected the experimental values, which are given relative to the Fermi level, by adding to them the photoelectric work function[24] in all cases except Rn which is a gas.

For the four elements considered, we find that the theoretical binding energies, which include all effects of $O(\alpha mc^2)$, agree to better than 0.4 Ry with the experimentally determined values. This is somewhat unexpected considering the fact that second- and higher-order effects have been neglected. Presumably, if these other effects are properly evaluated, they will account for part of the discrepancy; the remaining part will be due to numerical inaccuracies in our value of the self-energy.

Further corrections to the theoretical binding energy which should eventually be considered are (a) polarization corrections in the *K* ion which will have the effect of breaking the symmetry of the ion and will give direct (as contrasted with exchange) contributions to the magnetic energy of the ion; (b) higher-order corrections to the Breit interaction which are presently being investigated; preliminary results indicate that the higher-order corrections to the Breit interaction yield a combined shift of -0.44 Ry in the magnetic and retardation energies of Hg; this correction improves agreement between theory and experiment to 0.13 Ry for Hg; (c) higher-order αZ effects on vacuum polarization; techniques similar to those employed in Refs. 14 and 15 could, in principle, be applied to the vacuum-polarization calculation to obtain accurate (αZ) corrections to the Uehling potential values, as well as reliable estimates of nuclear size and screening corrections; (d) higher-order radiative corrections. These corrections which are of order $\alpha^2(\alpha Z)^4 mc^2$ would require an enormous amount of computation and probably will not be feasible until the next generation of computers.

It is difficult to estimate the validity of relating the experimentally measured binding energies in liquids and solids to the theoretical values in free atoms.[25] We have attempted to do so by adding experimentally determined work functions to the measured binding energies. Ideally, experiments should be performed on free atoms to make direct comparison possible. As an alternative, theoretical energy-level differences should be computed. This would have the effect of minimizing the solid-state effects in making comparison with experiment.

ACKNOWLEDGMENT

The authors are indebted to J. B. Mann of Los Alamos for communicating DHF values of the electrostatic and magnetic energies of the four elements studied.

---

*Research supported in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-427.

†Work based on a dissertation submitted in partial fulfillment of the requirements for the Ph. D. degree at the University of Notre Dame.

[1] D. Liberman, J. T. Waber, and D. T. Cromer [Phys. Rev. 137, A27 (1965)] quote D. F. Mayers.

[2] I. P. Grant, Proc. Roy. Soc. (London) A262, 555 (1961).

[3] G. E. Brown, D. F. Mayers, and E. A. Sanderson, Phys. Rev. Letters 3, 90 (1959).

[4] M. A. Coulthard, Proc. Phys. Soc. (London) 91, 44 (1967).

[5] A. Rosen and I. Lindgren, Phys. Rev. 176, 114 (1968).

[6] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. 39, 125 (1967).

[7] *Alpha-, Beta-, and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North Holland, Amsterdam, 1968), Appendix 2.

[8] J. M. Jauch and F. Rohrlich, *The Theory of Photons and Electrons* (Addison-Wesley, Reading, Mass., 1959), p. 306.

[9] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1957), p. 196.

[10] G. Breit, Phys. Rev. 34, 553 (1929); 36, 383 (1930); 39, 616 (1932).

[11] Y. K. Kim, Phys. Rev. 159, 17 (1967).

[12] H. A. Bethe and L. M. Brown, Phys. Rev. 77, 370 (1950).

[13] G. W. Erickson and O. R. Yennie, Ann. Phys. (N.Y.) 35, 271 (1965).

[14] G. E. Brown, J. S. Langer, and G. W. Schaefer, Proc. Roy. Soc. (London) A251, 92 (1959).

[15] G. E. Brown and D. F. Mayers, Proc. Roy. Soc. (London) A251, 105 (1959).

[16] E. H. Wichmann and N. M. Kroll, Phys. Rev. 101, 843 (1956).

[17] E. A. Uehling, Phys. Rev. 48, 55 (1935).

[18] T. Koopmans, Physica 1, 104 (1933).

[19] B. Hatlin, D. G. Ravenhall, and R. Hofstadter, Phys. Rev. 101, 1131 (1956).

[20] R. D. Cowan, Phys. Rev. 163, 54 (1967).

[21] This fact was pointed out to the authors by Professor I. Bialynicki-Birula.

[22] M. E. Rose, *Relativistic Electron Theory* (Wiley, New York, 1961), p. 27.

[23] A. I. Akhiezer and V. B. Berestetskii, *Quantum Electrodynamics* (Interscience, New York, 1965), p. 24.

[24] *Handbook of Thermionic Properties*, edited by G. V. Samsonov (Plenum, New York, 1966).

[25] J. C. Slater, Phys. Rev. 98, 1039 (1955).

PHYSICAL REVIEW A VOLUME 3, NUMBER 4 APRIL 1971

Cascade Effects in Certain Atomic Lifetime Measurements*

Roald K. Wangsness
Department of Physics, University of Arizona, Tucson, Arizona 85721

(Received 5 October 1970)

A semiclassical discussion is given of a simple case of the Hanle effect when the population of the level of interest varies with time because of decays to it from higher levels excited by collisions. It is found that the width of the intensity-vs-applied-field curve is no longer simply related to the lifetime of this single level, but depends on the relative populations and lifetimes of all other participating levels. It is shown by examples that, unless these effects are taken into account, the lifetimes deduced from the measurements can be greatly in error.

I. INTRODUCTION

Many of the methods used to measure lifetimes of excited atomic levels are based on the changes of intensity and polarization of the emitted light which occur when levels of different radiating properties are made degenerate, or nearly so, by varying an external parameter such as a magnetic field. Principal examples are various level-crossing experiments[1] and the Hanle effect (zero-field level crossing).[2] Observable effects are noted in a range of parameters corresponding to the overlap arising from the natural widths of the levels, thus enabling one to obtain information on the corresponding lifetimes.

A large number of these experiments are based on resonance fluorescence in which the system of interest is irradiated by light of the wavelength corresponding to the transition to be investigated. The incident light is usually broadened enough by the Doppler effect to ensure that the levels of interest are excited without, however, there being any danger that higher levels will also be excited. However, when excitation is produced by more