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Breit Interaction in Multielectron Atoms*

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The Breit interaction is reviewed with applications to heavy atoms in mind. Generalizations of the Breit interaction which avoid expansion in powers of the electron velocities are discussed. Two-particle matrix elements of the Breit interaction and its generalizations are given in a form convenient for numerical applications. Expressions are derived for evaluating configuration-averaged atomic energy shifts for the Breit interaction and its generalizations. Numerical results for the energy shifts of atomic ground states are presented for selected atoms in the range $Z=2$ to $Z=102$; interpolated values of the energy shifts are given graphically for all atoms in the range considered. A breakdown of the interelectron contributions to the Breit energy shift is given for Ne and for K electrons in Hg. "Frozen-orbital" calculations of Breit corrections to electron binding energies in Hg are given. The binding of K electrons in W, Hg, Pb, and Rn including the generalized Breit interaction with rearrangement are determined; when considered together with Lamb shift and correlation effects, these calculations reduce the discrepancy between theoretical and experimental K binding energies to about 0.1 Ry.

I. INTRODUCTION

The correction to the Coulomb repulsion between two electrons due to the exchange of a transverse photon is referred to as the Breit interaction.[1-3] In recent Dirac-Hartree-Fock (DHF) atomic-structure calculations one finds various related versions of the Breit interaction, leading to some confusion as to precisely what form the Breit correction takes in applications.

For example, Grant[4] takes the Breit interaction to be the unretarded interaction between two Dirac currents. Kim,[5] on the other hand, uses the retarded interaction proposed in Breit's original paper. A third version of the Breit interaction, derived from the retarded product of two four-currents, is used by Smith and Johnson.[6]

It is the purpose of the present paper to examine the various versions of the Breit interaction, both analytically and numerically, in order to elucidate the relations between the possible choices, and to give numerical tables of the energy shift associated with each possibility for free atoms.

Before proceeding further let us briefly review the history of the Breit interaction. In 1929, Gaunt[7] introduced a modification of the Coulomb interaction to account for the fine-structure separation in He. This correction, which we shall call the Gaunt interaction, is the unretarded interaction between two Dirac currents, and may be written[8]

$$H_G = -(\alpha/R)\,\vec{\alpha}_1\cdot\vec{\alpha}_2\,, \tag{1}$$

where α is the fine-structure constant, R is the interelectron separation, and $\vec{\alpha}_{1,2}$ are the usual Dirac matrices.

Later in 1929 Breit[1] pointed out that retardation effects on the charge-charge interaction, which are also of second order in the electron velocities, should be considered in parallel with the Gaunt interaction. The retardation interaction is given by

$$H_{\text{ret}} = (\alpha/2R)\,(\vec{\alpha}_1\cdot\vec{\alpha}_2 - \vec{\alpha}_1\cdot\vec{n}\,\vec{\alpha}_2\cdot\vec{n})\,, \tag{2}$$

where $\vec{n}$ is a unit vector along $\vec{R}$. The resulting interaction proposed by Breit is the sum of the two interactions given above:

$$H_{\text{Br}} = -(\alpha/2R)(\vec{\alpha}_1\cdot\vec{\alpha}_2 + \vec{\alpha}_1\cdot\vec{n}\,\vec{\alpha}_2\cdot\vec{n})\,. \tag{3}$$

In 1932 Breit[3] applied the interaction given in Eq. (3) to the problem of He fine structure and was as successful as Gaunt in predicting line separations.

In their studies of He, both Gaunt and Breit used the Pauli approximation to the two-electron Dirac equations. The Breit interaction in the Pauli approximation reduces to the familiar sum[9] of spin-orbit, spin-other-orbit, spin-spin, velocity-velocity, and Darwin terms. The corresponding decomposition of the Gaunt interaction gives identically the same spin-dependent terms but different velocity-velocity and Darwin terms. For the purpose of computing fine-structure separations in light atoms both interactions are therefore equivalent, explaining Gaunt's success in calculating He fine structure without retardation.

Using the Gaunt interaction to evaluate total energies in atoms is, of course, incorrect since the expectation of H_{ret} is generally nonzero. We shall see, however, from our numerical studies that H_G is typically an order of magnitude more important than H_{ret}, and even though retardation is not included in the Gaunt interaction, it still provides a useful approximation to the Breit interaction.

The Breit interaction can be understood from the point of view of quantum electrodynamics. The electromagnetic field is quantized in the transverse gauge, and the instantaneous Coulomb interactions are treated as classical fields. Neglecting the transverse field in the zeroth approximation, one constructs a DHF self-consistent field considering the mutual Coulomb interaction between electrons and the static nuclear potential. In the zeroth approximation one has the usual independent-particle description of the atom; the DHF energy of the atom is subject to the usual corrections due to Coulomb correlation effects.

Treating the transverse electromagnetic field in lowest-order perturbation theory, one may show that the interaction between any two atomic electrons due to the exchange of a single transverse photon is given by the nonlocal generalization of the Breit interaction,[10]

$$H'_{\text{Br}} = -\,\alpha\,\alpha_{1i}\,\alpha_{2j} \times \left[\delta_{ij}\,\frac{\cos\omega R}{R} + \frac{\partial^2}{\partial R_i\,\partial R_j}\,\frac{\cos\omega R - 1}{\omega^2 R}\right], \quad (4)$$

where ω is the energy transferred by the virtual photon. The first term in square brackets is the retarded version of the Gaunt interaction, while the second term is the retardation correction to the charge-charge interaction.

In direct two-electron matrix elements of H'_{Br} the photon energy $\omega = 0$; one sees by carrying out the limiting value of Eq. (4) that H'_{Br} reduces exactly to H_{Br}. In exchange matrix elements $\omega = \epsilon_1 - \epsilon_2$, the difference in orbital eigenvalues of the two electrons.

To the neglect of terms of order ω^2 (i.e., of fourth order in the electron velocities) the transverse interaction is identical to the Breit interaction. Thus, H'_{Br} provides the correction to Coulomb's law to lowest order in the fine-structure constant α arising from the exchange of a single transverse photon, while H_{Br} provides an approximation to H'_{Br} appropriate to the study of light atoms where electron velocities are small. For the inner electrons in heavy atoms, where electron velocities are of order $\alpha Z \sim 1$, one expects to find significant differences between matrix elements of H_{Br} and H'_{Br}.

An alternative version of H'_{Br} which is somewhat more convenient for computational purposes is given by[10-12]

$$H''_{\text{Br}} = -(\alpha/R)\left[\vec{\alpha}_1 \cdot \vec{\alpha}_2 \cos\omega R + (1 - \cos\omega R)\right]. \quad (4')$$

One can show that two-electron matrix elements of H'_{Br} and H''_{Br} are identical whenever the unperturbed electron orbitals satisfy Dirac equations in a *local potential.* Such situations arise, for example, when the electron-electron interaction can be neglected compared with the electron-nucleus interaction or when a local approximation to the electron-electron interaction such as the Dirac-Hartree-Fock-Slater (DHFS) approximation can be made. It must be emphasized, however, that H'_{Br} rather than H''_{Br} is the interaction appropriate to the DHF description of the unperturbed atom, and that the matrix elements of H'_{Br} and H''_{Br} are *not* identical when evaluated using DHF electron orbitals.

In the above discussion the Breit interaction is seen to follow from quantum electrodynamics in *first-order perturbation theory.* Using the interaction to determine the self-consistent field, or using the interaction in second- or higher-order perturbation theory, is incorrect and has, in the past, led to both logical[13] and numerical[2,3] difficulties.

We are now in a position to comment on the problem posed at the beginning of the paper. First, it is clear that the transverse interaction H'_{Br} of Eq. (4) is the version of the correction to Coulomb's law appropriate for use as a perturbation in DHF calculations. For light elements, where $\alpha Z \ll 1$, the Breit interaction H_{Br} of Eq. (3) is expected to be in error by terms of relative order $(\alpha Z)^2$. To the extent that such errors are negligible in atomic-structure calculations, the Breit interaction may be used to replace H'_{Br}. This is the situation in the atomic-structure calculations of Kim.[5]

The Gaunt interaction of Eq. (1) neglects retardation effects which influence exchange matrix elements only. As mentioned previously, the energy shifts resulting from H_G are larger by an order of magnitude than those due to retardation. The Gaunt interaction used by Grant[4] thus provides an approximation to H_{Br} suitable not only for fine-structure calculations but also for the approximate evaluation of magnetic energy shifts.

The interaction H''_{Br}, which was used in the atomic-structure calculations of Smith and Johnson,[6] is the version of H_{Br} appropriate to an unperturbed theory involving a local potential. In particular, this version of the interaction provides a useful approximation for the study of the inner electrons of heavy atoms where the nuclear potential dominates the interelectron interaction.

It should be mentioned in passing that Grant[4] and Smith and Johnson[6] use the Breit interaction to determine the self-consistent field. As pointed out above, such a procedure is incorrect; Kim's treatment of H_{Br} in first-order perturbation theory represents the correct procedure for handling H_{Br} in applications.

To discuss the energy shift induced in atoms by the Breit interaction we must compute matrix elements of the operators in Eqs. (1)–(4) above. Such calculations already occur for H_G in Grant's paper[4] and for H_{ret} in Kim's paper.[5] In Sec. II we give an alternative derivation of the matrix elements of H_G, H_{ret}, and H_{Br} which parallels the previous calculations of Refs. 4 and 5. The technique developed in Sec. II is applied in Sec. III to evaluate matrix elements of H'_{Br} and H''_{Br}. Interestingly, we are able to extract from the matrix elements of H''_{Br} expressions for the matrix elements of H_{ret}, applicable in the case of a local potential, which are considerably simpler than those given by Kim.[5]

In Sec. IV we apply the formulas derived in Secs. II and III to the study of the Breit interaction in atoms. We find for light atoms energy corrections due to the Breit interaction which are different from those given by Kim.[5] For heavy atoms it is found that the Gaunt interaction dominates the Breit interaction and that the differences between the Breit interaction and its generalization H'_{Br} are significant for the heaviest atoms.

II. MATRIX ELEMENTS OF BREIT INTERACTION

We consider the decomposition $H_{\mathrm{Br}} = H_G + H_{\mathrm{ret}}$ and evaluate separately the DHF matrix element of each term. There are two reasons for proceeding in this fashion. First, as we show in the numerical calculations of Sec. IV, the energy shift associated with H_G is larger than that associated with H_{ret} by an order of magnitude. Second, in the previous literature separate calculations of H_G[4,5] and H_{ret}[5] appear, which provide useful checks on the present work.

In the previous calculations some rather difficult questions of angular momentum recoupling were faced, leading to expressions for the magnetic and retardation energies involving Racah coefficients and 9-j symbols. It is the purpose of the present section to illustrate a technique for calculating the interaction energy without explicit use of the Racah algebra. This technique is then applied in Sec. III to evaluate the matrix elements of H'_{Br}.

A. Matrix Elements of H_G

Since H_G is a two-electron operator, the energy shift for an atomic system is the sum over pairs of two-electron matrix elements E^G_{AB}. Each two-electron matrix element is in turn the sum of a direct and an exchange term. We write

$$E^G_{AB} = K^G_{AB} + L^G_{AB}\ , \tag{5}$$

with

$$\begin{aligned} K^G_{AB} &= -\alpha\int \frac{d^3r_1\, d^3r_2}{R}\,(u^\dagger_A\vec{\alpha}_1 u_A)\cdot(u^\dagger_B\vec{\alpha}_2 u_B)\ , \\ L^G_{AB} &= \alpha\int \frac{d^3r_1\, d^3r_2}{R}\,(u^\dagger_B\vec{\alpha}_1 u_A)\cdot(u^\dagger_A\vec{\alpha}_2 u_B)\ , \end{aligned} \tag{6}$$

where u_A and u_B designate four-component DHF orbitals of electrons A and B.

The DHF orbitals have the central field form

$$u(\vec{\mathrm{r}}) = \frac{1}{r}\begin{pmatrix} i\,G(r)\,\Omega_{\kappa m}(\hat{r}) \\ F(r)\,\Omega_{-\kappa m}(\hat{r}) \end{pmatrix}\ . \tag{7}$$

The radial functions $G(r)$ and $F(r)$ are the large and small components, respectively, of the Dirac wave function $u(\vec{r})$; they are assumed to satisfy central field radial DHF equations.[14] The symbol $\Omega_{\kappa m}(\hat{r})$ is used to designate a spherical spinor[15] of angular momentum j, projection m, and orbital angular momentum l; the parameter $\kappa = \mp(j+\frac{1}{2})$ for $j = l \pm \frac{1}{2}$. The one-electron orbitals are completely specified by giving the value of κ and m together with a principal quantum number n.

We are faced with the evaluation of vector expressions such as $(u^\dagger_B\vec{\alpha}u_A)$. To facilitate calculations with such expressions we expand in terms of vector spherical harmonics. Let $Y_{JLM}(\hat{r})$ designate the vector spherical harmonic[16] formed by combining a unit-spin spherical basis vector with a spherical harmonic of order L to give angular momentum $J = L,\ L \pm 1$. Writing

$$(u^\dagger_B\vec{\alpha}u_A) = -\frac{i}{r^2}\sum_{JLM} C_{JLM}(r)\,Y_{JLM}(\hat{r})\ , \tag{8}$$

one finds

$$\begin{aligned} C_{JJ-1M} &= I_J(\kappa_A m_A,\ \kappa_B m_B)\,[J/(2J+1)]^{1/2}\,P_{AB}(r)\ , \\ C_{JJM} &= I_J(-\kappa_A m_A,\ \kappa_B m_B) \\ &\qquad \times (\kappa_A+\kappa_B)\,[J(J+1)]^{-1/2}\,V_{AB}(r)\ , \\ C_{JJ+1M} &= I_J(\kappa_A m_A,\ \kappa_B m_B) \\ &\qquad \times [(J+1)/(2J+1)]^{1/2}\,Q_{AB}(r)\ , \end{aligned} \tag{9}$$

with

$$\begin{aligned} P_{AB}(r) &= U_{AB}(r) + [(\kappa_B-\kappa_A)/J]\,V_{AB}(r)\ , \\ Q_{AB}(r) &= -U_{AB}(r) + [(\kappa_B-\kappa_A)/(J+1)]\,V_{AB}(r)\ , \\ U_{AB}(r) &= G_A(r)\,F_B(r) - F_A(r)\,G_B(r)\ , \\ V_{AB}(r) &= G_A(r)\,F_B(r) + F_A(r)\,G_B(r)\ . \end{aligned} \tag{10}$$

In the above we have used

$$I_J(\kappa_A m_A,\ \kappa_B m_B) = \int \Omega^\dagger_{\kappa_A m_A}\,Y_{JM}\,\Omega_{\kappa_B m_B}\,d\Omega$$

$$= (-1)^{J+j_B-j_A}\left(\frac{(2J+1)(2j_B+1)}{4\pi(2j_A+1)}\right)^{1/2} C(j_B J j_A;\tfrac{1}{2}0)\,C(j_B J j_A; m_B M m_A)\,\Pi(l_A J l_B)\ . \tag{11}$$

The Clebsch-Gordan coefficients occurring in Eq. (11) guarantee that $j_A + j_B \geqslant J \geqslant |j_A - j_B|$ and that $M = m_A - m_B$, while the factor

$$\Pi(l_A J l_B) = \begin{cases} 1 \text{ for } l_A + J + l_B \text{ even} \\ 0 \text{ for } l_A + J + l_B \text{ odd} \end{cases}$$

restricts the allowed J values by parity conservation. When κ is replaced by $-\kappa$ in either argument of Eq. (11), the values of J permitted by the parity selection factor change by one unit since $l(-\kappa) = l(\kappa) \pm 1$.

All of the complications of angular momentum recoupling are now contained in the one coefficient $I_J(\kappa_A m_A,\ \kappa_B m_B)$.

Let us apply the expansion (8) to evaluate the direct contribution to the magnetic energy. We write

$$(u_A^\dagger \vec{\alpha}_1 u_A) = -\frac{i}{r_1^2}\sum_J D_J^A(r_1)\, Y_{JJ0}(\hat{r}_1)\ , \tag{12}$$

$$(u_B^\dagger \vec{\alpha}_2 u_B) = \frac{i}{r_2^2}\sum_J D_J^B(r_2)\, Y^\dagger_{JJ0}(\hat{r}_2)\ , \tag{13}$$

where D_J^A and D_J^B are obtained from the general expansion (9). Notice that the vector harmonics for $L = J \pm 1$ are absent from expansions (12) and (13), and that only the $M = 0$ terms contribute.

Substituting Eqs. (12) and (13) into the expression (6) for the direct magnetic energy, and making use of the well-known expansion of $1/R$ in spherical harmonics, one finds

$$K_{AB}^G = -\alpha\sum_J c_J(\kappa_A m_A,\ \kappa_B m_B)\frac{4\kappa_A\kappa_B}{J(J+1)}\, S_{AB}^J\ , \tag{14}$$

where the Slater-type integral S_{AB}^J is defined by

$$S_{AB}^J = \int_0^\infty dr_1 \int_0^\infty dr_2\, \frac{r_<^J}{r_>^{J+1}}\, V_{AA}(r_1)\, V_{BB}(r_2)\ , \tag{15}$$

and where

$$c_J(\kappa_A m_A,\ \kappa_B m^B) = 4\pi(2J+1)^{-1} I_J(-\kappa_A m_A,\ \kappa_A m_A) \times I_J(-\kappa_B m_B,\ \kappa_B m_B)\ . \tag{16}$$

Parity selection limits J to odd values in Eq. (14).

Substituting Eq. (8) and its conjugate into the expression for L_{AB}^G in Eq. (6) and performing the angular integrations as before, we find

$$L_{AB} = \alpha\sum_J \left\{ b_J(\kappa_A m_A,\ \kappa_B m_B)\left[\frac{J}{2J-1}\, T_{AB}^{J,J-1} + \frac{J+1}{2J+3}\, T_{AB}^{J,J+1}\right] + b_J(-\kappa_A m_A,\ \kappa_B m_B)\frac{(\kappa_A+\kappa_B)^2}{J(J+1)}\, T_{AB}^{J,J}\right\}\ , \tag{17}$$

where

$$T_{AB}^{J,J-1} = \int_0^\infty dr_1 \int_0^\infty dr_2\, \frac{r_<^{J-1}}{r_>^{J}}\, P_{AB}(r_1)\, P_{AB}(r_2)\ ,$$

$$T_{AB}^{J,J+1} = \int_0^\infty dr_1 \int_0^\infty dr_2\, \frac{r_<^{J+1}}{r_>^{J+2}}\, Q_{AB}(r_1)\, Q_{AB}(r_2)\ , \tag{18}$$

$$T_{AB}^{J,J} = \int_0^\infty dr_1 \int_0^\infty dr_2\, \frac{r_<^{J}}{r_>^{J+1}}\, V_{AB}(r_1)\, V_{AB}(r_2)\ ,$$

and where

$$b_J(\kappa_A m_A,\ \kappa_B m_B) = 4\pi(2J+1)^{-1} I_J^2(\kappa_A m_A,\ \kappa_B m_B)\ . \tag{19}$$

The three terms in brackets in Eq. (17) correspond to the three possibilities $L = J,\ J \pm 1$.

At this point we are able to make a direct comparison of our expressions for the matrix element of the Gaunt interaction with that given by Grant.[4] We find that Eqs. (14) and (17) provide a rearranged version of the corresponding expressions in Ref. 4, with the virtue that averages over atomic subshells are now extremely simple.

B. Matrix Elements of $H_{\rm ret}$

We now turn to the somewhat more involved problem of evaluating the two-electron matrix element of $H_{\rm ret}$. We again decompose the corresponding matrix element $E_{AB}^{\rm ret}$ into a direct term K and an exchange term L; $E_{AB}^{\rm ret} = K_{AB}^{\rm ret} + L_{AB}^{\rm ret}$, where $K_{AB}^{\rm ret}$ and $L_{AB}^{\rm ret}$ are given by expressions similar to Eqs. (6) with $-\vec{\alpha}_1 \cdot \vec{\alpha}_2/R$ replaced by $(\vec{\alpha}_1 \cdot \vec{\alpha}_2 - \vec{\alpha}_1 \cdot \mathrm{n}\, \vec{\alpha}_2 \cdot \mathrm{n})/2R$.

We will show that the direct matrix element of $K_{AB}^{\rm ret}$ vanishes. Before we do this it is somewhat more convenient to look at the exchange matrix element $L_{AB}^{\rm ret}$. To evaluate the exchange contribution to the retardation energy we employ the identity

$$\frac{\delta_{ij} - n_i n_j}{R} = \frac{\partial^2 R}{\partial x_{1i}\,\partial x_{1j}} = -2\lim_{\mu\to 0}\frac{\partial^2}{\partial x_{1i}\,\partial x_{1j}}\,\frac{\cos\mu R - 1}{\mu^2 R}\ , \tag{20}$$

where the x_{1i} are components of the coordinate of particle 1. We may then write

$$L_{AB}^{\rm ret} = \alpha\int d^3 r_1\, (u_A^\dagger \vec{\alpha}_1 u_B) \cdot \lim_{\mu\to 0} \vec{\nabla}_1 (\vec{\nabla}_1 \cdot \vec{\mathrm{J}})\ , \tag{21}$$

where

$$\vec{\mathrm{J}}(\vec{\mathrm{r}}_1,\ \mu) = \int d^3 r_2\, (u_B^\dagger \vec{\alpha}_2 u_A)\, \frac{\cos\mu R - 1}{\mu^2 R}\ . \tag{22}$$

Now making use of the expansion (8), and expressing $\cos(uR)/R$ in terms of spherical harmonics,[17] we find

$$\vec{J}(\vec{r}_1, \mu) = 4\pi i \sum_{JLM} R_{JLM}(r_1, \mu)\, Y_{JLM}(\hat{r}_1) \,, \tag{23}$$

where

$$R_{JLM}(r_1, \mu) = \frac{1}{\mu^2}\int_0^\infty dr_2\, C_{JLM}(r_2) \times \left[\mu j_L(\mu r_<)\, y_L(\mu r_>) + \frac{1}{(2L+1)} \frac{r_<^L}{r_>^{L+1}} \right], \tag{24}$$

j_L and y_L being spherical Bessel functions of the first and second kinds.

Carrying out the differentiations and the limit indicated in Eq. (21), one arrives at the following result:

$$L_{AB}^{\mathrm{ret}} = -\alpha \sum_J b_J(\kappa_A m_A, \kappa_B m_B) \left\{ \frac{J^2}{(2J+1)(2J-1)}\, T_{AB}^{J,J-1} + \frac{(J+1)^2}{(2J+1)(2J+3)}\, T_{AB}^{J,J+1} + \frac{J(J+1)}{2J+1}\, X_{AB}^J \right\}, \tag{25}$$

where the angular coupling coefficients b_J and the Slater-type integrals $T_{AB}^{J,L}$ have been previously defined, and where

$$X_{AB}^J = \int_0^\infty dr_1 \int_0^{r_1} dr_2 \left(\frac{r_<^{J-1}}{r_>^J} - \frac{r_<^{J+1}}{r_>^{J+2}} \right) Q_{AB}(r_1)\, P_{AB}(r_2) \,. \tag{26}$$

To see that the direct matrix element K_{AB}^{ret} vanishes let us apply the identity (20) to the retardation matrix element. We obtain an expression similar to Eq. (21),

$$K_{AB}^{\mathrm{ret}} = -\alpha \int d^3 r_1 (u_B^\dagger \vec{\alpha}_1 u_B) \cdot \lim_{\mu\to 0} \vec{\nabla}_1 (\vec{\nabla}_1 \cdot \vec{J}) \,, \tag{21$'$}$$

where $\vec{J}$ is given by Eq. (22) with $(u_B^\dagger \vec{\alpha} u_A)$ replaced by $(u_A^\dagger \vec{\alpha} u_A)$. Expanding $\vec{J}$ in vector spherical harmonics as in Eq. (23), we find now [see Eq. (12)] that only the terms $L = J$, $M = 0$ contribute to the summation. Using the fact that $\vec{\nabla} \cdot f(r) \vec{Y}_{JJ0}(\hat{r}) = 0$, one immediately sees that $K_{AB}^{\mathrm{ret}} \equiv 0$.

The expression (25) for the retardation energy can be compared with the corresponding expression given by Kim.[5] Again, we arrive at a rearranged version of the results of Ref. 5 which may be averaged over subshells in an essentially trivial manner.

We have now arrived at expressions for the two-electron matrix elements of the Gaunt and retardation interactions in terms of Slater-type radial integrals and angular coupling coefficients. Next, we turn to the problem of developing expressions for the energy shift of an entire atom by summing the two-electron contribution to the interaction energy over all pairs of atomic electrons.

C. Spherically Averaged Breit Interaction

The two-electron matrix element of H_{Br} has been decomposed into three terms,

$$E_{AB}^{\mathrm{Br}} = K_{AB}^G + L_{AB}^G + L_{AB}^{\mathrm{ret}} \,.$$

In our applications we consider situations in which the radial Dirac functions are independent of the projection quantum number m. For such cases we are interested in the average of the Breit interaction over subshells with a fixed value of n and κ.

If electrons $A = (n_A, \kappa_A, m_A)$ and $B = (n_B, \kappa_B, m_B)$ are in distinct subshells $n_A \neq n_B$ or $\kappa_A \neq \kappa_B$, one has for the average two-electron interaction

$$\overline{E}_{AB} = [(2j_A+1)(2j_B+1)]^{-1} \sum_{m_A, m_B} E_{AB} \,, \tag{27}$$

where the summation extends over the $2j+1$ possible m values.

For two electrons in the same subshell, $n_B = n_A$ and $\kappa_B = \kappa_A$, one has for the average interaction energy

$$\overline{E}_{AA} = [2j_A(2j_A+1)]^{-1} \sum_{m_A, m_B} E_{AB} \,. \tag{28}$$

The resulting average interaction energies are functions of the subshell parameters n and κ only.

One easily establishes that $\overline{K}_{AB}^G = 0$; i.e., that the direct contribution to the Gaunt interaction vanishes upon averaging over subshells. This follows from the fact that

$$\sum_{m_A} c_J(\kappa_A m_A, \kappa_B m_B) = 0 \,. \tag{29}$$

One further establishes that

$$\sum_{m_A} b_J(\pm\kappa_A m_A, \kappa_B m_B) = (2j_A+1)\,\Lambda_J(\kappa_A, \kappa_B) \,, \tag{30}$$

where

$$\Lambda_J(\kappa_A, \kappa_B) = (2j_B+1)^{-1} C^2(j_A J j_B\,;\, \tfrac{1}{2}0)\, \Pi(l_A J l_B) \,. \tag{31}$$

Notice that the allowed values of J for $+\kappa_A$ and $-\kappa_A$ differ by one unit because of the parity factor Π. The factor $\Lambda_J(\kappa_A, \kappa_B)$ is related to the corresponding angular coupling coefficient $\Gamma_{j_A J j_B}$ used by Grant[4] to evaluate electrostatic interactions by

$$\Lambda_J(\kappa_A, \kappa_B) = \tfrac{1}{2}\Gamma_{j_A J j_B}\, \Pi(l_A J l_B) \,. \tag{31$'$}$$

We may now write the spherically averaged Breit interaction energy for an atomic system as

$$\overline{E}_{\mathrm{Br}} = \sum_{[A],[B]}{}' q_A q_B (\overline{L}_{AB}^G + \overline{L}_{AB}^{\mathrm{ret}})$$

$$+\tfrac{1}{2}\sum_{[A]} q_A\,(q_A-1)\,\frac{2j_A+1}{2j_A}\,\overline{L}{}^{G}_{AA}\ . \qquad (32)$$

The first summation over distinct subshell pairs $[A]=(n_A,\ \kappa_A)$ and $[B]=(n_B,\ \kappa_B)$ represents the intershell contributions to the energy shift, while the second summation over $[A]$ gives the intrashell contributions. The symbols q_A and q_B represent the number of electrons in shells $[A]$ and $[B]$. The average values of the Gaunt and retardation contributions are given by

$$\overline{L}{}^{G}_{AB}=\alpha\sum_J\left\{\Lambda_J(\kappa_A,\ \kappa_B)\left[\frac{J}{2J-1}\,T^{J,J-1}_{AB}+\frac{J+1}{2J+3}\,T^{J,J+1}_{AB}\right]+\Lambda_J(-\kappa_A,\ \kappa_B)\,\frac{(\kappa_A+\kappa_B)^2}{J(J+1)}\,T^{J,J}_{AB}\right\} \qquad (17')$$

and

$$\overline{L}{}^{\mathrm{ret}}_{AB}=-\alpha\sum_J\Lambda_J(\kappa_A,\ \kappa_B)\left[\frac{J^2}{(2J+1)\,(2J-1)}\,T^{J,J-1}_{AB}+\frac{(J+1)^2}{(2J+1)\,(2J+3)}\,T^{J,J-1}_{AB}+\frac{J(J+1)}{2J+1}\,X^{J}_{AB}\right]. \qquad (25')$$

In Eq. (32) we have dropped the term $\overline{L}{}^{\mathrm{ret}}_{AA}$, which is easily seen to vanish. The corresponding average of the Gaunt interaction within a shell is

$$\overline{L}{}^{G}_{AA}=\alpha\sum_J\Lambda_J(-\kappa_A,\ \kappa_A)\,\frac{4\kappa_A^2}{J(J+1)}\,T^{J,J}_{AA}\ . \qquad (17'')$$

In Sec. III we apply the techniques developed above to the problem of evaluating the matrix element of H'_{Br} and H''_{Br}.

III. MATRIX ELEMENTS OF GENERALIZED BREIT INTERACTION

A. Reduction of H'_{Br}

In parallel with the decomposition $H_{\mathrm{Br}}=H_G+H_{\mathrm{ret}}$, we write $H'_{\mathrm{Br}}=H'_G+H'_{\mathrm{ret}}$, with

$$H'_G=-\,(\alpha/R)\,\vec{\alpha}_1\cdot\vec{\alpha}_2\,\cos\omega R\ ,$$

$$H'_{\mathrm{ret}}=-\,\alpha\,\alpha_{1i}\,\alpha_{2j}\,\frac{\partial^2}{\partial R_i\,\partial R_j}\,\frac{\cos\omega R-1}{\omega^2 R}\ . \qquad (33)$$

To evaluate direct two-electron matrix elements K'^{G}_{AB} and K'^{ret}_{AB} we set $\omega=0$, and recall from the discussion following Eq. (4) that H'_{Br} reduces to H_{Br}. We therefore have

$$K'^{G}_{AB}=K^{G}_{AB}\ ,\quad K'^{\mathrm{ret}}_{AB}=K^{\mathrm{ret}}_{AB}=0\ . \qquad (34)$$

For exchange matrix elements L'^{G}_{AB} and L'^{ret}_{AB}, where $\omega=\epsilon_A-\epsilon_B$, we proceed in the manner outlined in Sec. II. In evaluating L'^{G}_{AB} the principal difference which arises is that one must replace the expansion of $1/R$ into spherical harmonics with the corresponding expansion of $\cos(\omega R)/R$. The result of such a replacement is that the factors $r_<^L/r_>^{L+1}$ which occur in the Slater integrals $T^{J,L}_{AB}$ are now replaced by products of spherical Bessel functions:

$$\frac{r_<^L}{r_>^{L+1}}\to-\,\omega(2L+1)j_L\,(\omega r_<)\,y_L(\omega r_>)\ . \qquad (35)$$

It follows that L'^{G}_{AB} is given by Eq. (17), with the proviso that the Slater integrals $T^{J,L}_{AB}$ of Eqs. (18) be modified by the replacement (35). We express this symbolically as

$$L'^{G}_{AB}=L^{G}_{AB}\,(T'^{J,L}_{AB})\ ,$$

$$T'^{J,L}_{AB}=T^{J,L}_{AB}\,[\,r_<^L/r_>^{L+1}\to-\,\omega(2L+1)j_L\,(\omega r_<)\times y_L\,(\omega r_>)]\ . \qquad (36)$$

One easily shows that the limiting value for $\omega\to0$ of the right-hand side of (35) is exactly $r_<^L/r_>^{L+1}$. Thus, L'^{G}_{AB} reduces to L^{G}_{AB} to neglect of retardation effects on the current-current interaction.

To obtain the exchange matrix element of H'_{ret} we notice that L'^{ret}_{AB} is given by Eqs. (21) and (22) provided the parameter μ is replaced by ω and the limit in Eq. (21) is disregarded. By following the steps outlined after Eq. (22) of Sec. II B, one is led to a modification of Eq. (25) which can be expressed symbolically as

$$L'^{\mathrm{ret}}_{AB}=L^{\mathrm{ret}}_{AB}\,(T'^{J,L}_{AB},\ X'^{J}_{AB})\ , \qquad (37)$$

where $T'^{J,L}_{AB}$ is given in terms of $T^{J,L}_{AB}$ as in Eq. (36), and where X'^{J}_{AB} is given by the following rather complicated generalization of Eq. (26):

$$X'^{J}_{AB}=\int_0^\infty dr_1\int_0^{r_1}dr_2\left\{-2\left(\omega j_{J-1}\,(\omega r_<)\,y_{J+1}\,(\omega r_>)+\frac{2J+1}{\omega^2}\,\frac{r_<^J}{r_>^{J+1}}\right)Q_{AB}(r_1)\,P_{AB}(r_2)-2\omega\,j_{J+1}\,(\omega r_<)\,y_{J-1}\,(\omega r_>)\,P_{AB}(r_1)\,Q_{AB}(r_2)\right\}. \qquad (38)$$

As $\omega\to0$ the expression (38) reduces identically to (26) and L'^{ret}_{AB} reduces to L^{ret}_{AB}.

All of the formulas of Sec. IIC for the average energy shifts apply to the present case also provided the unprimed quantities are replaced by the corresponding primed expressions.

B. Reduction of H''_{Br}

We now turn to the problem of evaluating matrix elements of the modified interaction H''_{Br}, which, as noted in the Introduction, is equivalent to H'_{Br} for cases in which the unperturbed orbitals $u_A(r)$ satisfy local-potential Dirac equations. We again write $H''_{\mathrm{Br}} = H''_G + H''_{\mathrm{ret}}$, with

$$H''_G = H'_G = -(\alpha/R)\vec{\alpha}_1 \cdot \vec{\alpha}_2 \cos\omega R \ ,$$
$$H''_{\mathrm{ret}} = (\alpha/R)(\cos\omega R - 1) \ . \tag{39}$$

Since $H''_G = H'_G$, one has immediately that the direct and exchange matrix elements of H''_G (K''^G_{AB} and L'^G_{AB}) are identical to those of H'_G:

$$K''^G_{AB} = K'^G_{AB} = K^G_{AB} \ , \quad L''^G_{AB} = L'^G_{AB} \ , \tag{40}$$

and we need only evaluate matrix elements of H''_{ret}.

Direct matrix elements of H''_{ret} vanish, as expected, since in direct terms $\omega = 0$ and the operator $H''_{\mathrm{ret}} = 0$. Thus

$$K''^{\mathrm{ret}}_{AB} = 0. \tag{41}$$

To obtain the exchange matrix element of H''_{ret} one uses the expansion

$$(u^\dagger_B u_A) = \frac{1}{r^2} \sum_{JM} I_J(\kappa_A m_A, \kappa_B m_B) \times W_{AB}(r)\, Y_{AB}(\hat{r}) \ , \tag{42}$$

with $W_{AB} = G_A G_B + F_A F_B$. Expanding $(\cos\omega R - 1)/R$ in terms of spherical harmonics and carrying out the angular integrations, one obtains

$$L''^{\mathrm{ret}}_{AB} = \alpha \sum_J b_J(\kappa_A m_A, \kappa_B m_B)\, Y^J_{AB} \ , \tag{43}$$

where the Slater integral Y^J_{AB} is given by

$$Y^J_{AB} = \int_0^\infty dr_1 \int_0^\infty dr_2 \left[\frac{r^J_<}{r^{J+1}_>} + \omega(2J+1) j_{LJ}(\omega r_<) \times y_J(\omega r_>)\right] W_{AB}(r_1)\, W_{AB}(r_2) \ . \tag{44}$$

The integral Y^J_{AB} has the form of an electrostatic exchange integral with $r^J_</r^{J+1}_>$ replaced by the more complicated expression in square brackets. Equation (43) has obvious computational advantages over the corresponding expression (37) and should be used whenever the local-potential assumption is satisfied.

As $\omega \to 0$ the integrand in Eq. (44) vanishes and we have no retardation. Expanding the integrand to lowest nonvanishing order in ω, we find

$$Y_{AB} \cong -\frac{\omega^2}{2} \int_0^\infty dr_1 \int_0^\infty dr_2 \left[\frac{r^J_<}{(2J-1)\, r^{J-1}_>} - \frac{r^{J+2}_<}{(2J+3)\, r^{J+1}_>}\right] W_{AB}(r_1)\, W_{AB}(r_2) \ . \tag{45}$$

Substituting Eq. (45) into Eq. (43) gives a simple alternative to Eq. (25) for L^{ret}_{AB} applicable in local-potential cases.

Again we may take over the results of Sec. IIC for average interaction energies, now replacing unprimed expressions by the corresponding double-primed quantities, provided we replace $\bar{L}^{\mathrm{ret}}_{AB}$ by the average of L''^{ret}_{AB}, which is given by

$$\bar{L}''^{\mathrm{ret}}_{AB} = \alpha \textstyle\sum_J \Lambda_J(\kappa_A, \kappa_B)\, Y^J_{AB} \ . \tag{46}$$

In Sec. IV we present numerical studies of E_{Br} and E'_{Br} for the ground state of various atoms, to illustrate the size of the magnetic energy shift as well as the range of atomic numbers for which the Breit interaction H_{Br} provides an accurate approximation to H'_{Br}.

IV. NUMERICAL STUDIES OF BREIT INTERACTION

To apply the Breit interaction to particular atoms it is first necessary to have the unperturbed radial DHF wave functions G_A and F_A of Eq. (7) for the various subshells of the atoms under consideration. In the studies presented below these unperturbed wave functions were generated numerically using a computer program written by one of us (J. B. M.). A discussion of the formulation and solution of the radial DHF equations is given by Mann and Waber.[18] Several points concerning the unperturbed wave functions should be kept in mind when viewing the numerical results below.

First, it should be noted that the nuclear potential used in the DHF problem includes nuclear finite size effects; the potential is determined from a Fermi-charge distribution with parameters given by electron scattering data. The resulting zeroth-order energies and inner-shell binding energies are reduced in magnitude from the corresponding point nucleus DHF values; the reduction in size is particularly noticeable for the heavier elements. The radial wave functions G_A and F_A for the finite nucleus potential do not have the characteristic Coulomb singularity at $r = 0$.

A second point which should be kept in mind is that the value of the fine-structure constant α used in the unperturbed DHF calculation of Ref. 18, and below, is an older value, $\alpha^{-1} = 137.039$. Since both the Gaunt and retardation energies are proportional to α^2 in the lowest approximation, one expects changes in the relative size of both energies of $\Delta E/E \approx 2\Delta\alpha/\alpha$ due to changes in the value of α. Using a more recent value,[19] $\alpha^{-1} = 137.0360$, one therefore expects an increase in the relative magnitude of the various Breit interaction energies presented in the following tables of approximately 4.4×10^{-5}; the same increase is also expected in the relativistic part of the unperturbed DHF energies.

The Breit interaction and the general transverse interaction were evaluated for various $J = 0$ atomic ground states from He ($Z = 2$) to No ($Z = 102$) using the formulas developed in the preceding sections.

In Table I we present the results of this numerical evaluation. Column 3 gives the DHF energy, which of course includes the effects of the (finite) nuclear potential and of the electrostatic interelectron interactions. The last two columns list the Gaunt and retardation contributions to the Breit interaction. One sees the increase in relative importance of these magnetic and retardation effects with increasing Z. It is interesting to note that the energy shift due to retardation is about 10% of the Gaunt energy shift throughout the range considered, and that the Gaunt and retardation contributions are of opposite signs. This can be compared with a free-electron gas in which the retardation energy is $-\frac{1}{6}$ of the Gaunt energy.

The present Breit interaction results for He, Be, and Ne can be compared with the values given by Kim[5]: $E^G(\mathrm{He}) = 0.00016$ Ry, $E^{\mathrm{ret}}(\mathrm{He}) = 0.0$; $E^G(\mathrm{Be}) = 0.00232$ Ry, $E^{\mathrm{ret}}(\mathrm{Be}) = -0.000008$ Ry; and $E^G(\mathrm{Ne}) = 0.0262$ Ry, $E^{\mathrm{ret}}(\mathrm{Ne}) = -0.0024$ Ry. While the sign and magnitude of our terms agree with those of Ref. 5, the actual numerical values are in serious disagreement except for $E^{\mathrm{ret}}(\mathrm{Be})$ (see Ref. 19a).

Columns 4 and 5 of Table I give our results for the transverse interaction energy. It is seen that the effect of the higher-order αZ terms is to reduce the magnitude of both the Gaunt and retardation energies. For atoms with $Z < 48$ the Breit and transverse energies agree to within 1 eV, while the discrepancy becomes increasingly more significant for larger atomic numbers.

The rate of growth of the various terms listed in Table I can be seen clearly in the graph of energy versus atomic number in Fig. 1. The DHF energy is found to grow approximately as $Z^{2.4}$; both the Gaunt and, for high Z, retardation contributions to the transverse interaction are approximately proportional to $Z^{3.6}$.

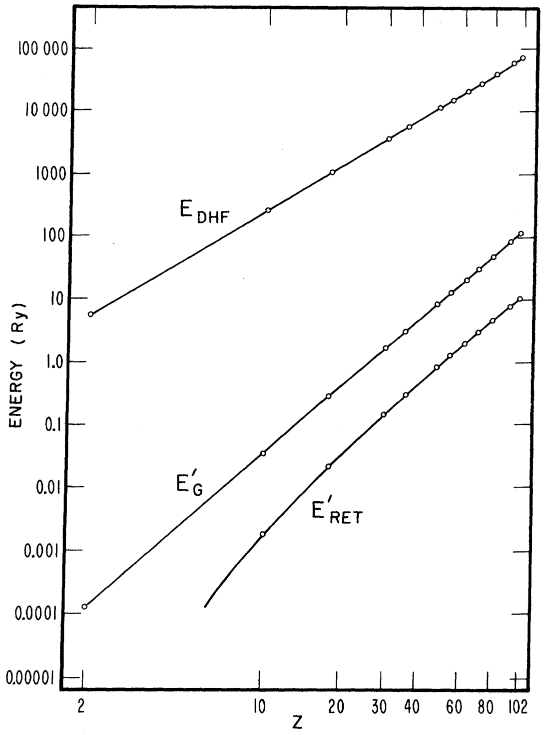

FIG. 1. DHF, Gaunt, and retardation energies for the ground state of atoms. The DHF energy behaves approximately as $Z^{2.4}$, while the Gaunt and retardation energies vary approximately as $Z^{3.6}$.

To understand the size of the various contributions to the Gaunt and retardation energies we list in Table II a detailed breakdown of the average interaction for all subshells of Ne and for the K shell of Hg. In column 2 we list $\overline{L}'^{G}_{AB}$, the average value

TABLE I. Comparison of Breit interaction energy with transverse interaction energy for the ground states of selected atoms. The value E_{DHF} is the unperturbed DHF ground-state energy. Energies in Ry units.

			Transverse interaction		Breit interaction	
Element	Z	E_{DHF}	E'_G	E'_{ret}	E_G	E_{ret}
He	2	−5.7236	0.00013	−0.	0.00013	−0
Be	4	−29.1518	0.00141	−0.000008	0.00141	−0.000008
Ne	10	−257.3838	0.03507	−0.00179	0.03508	−0.00180
A	18	−1057.3673	0.28636	−0.02194	0.28686	−0.02214
Zn	30	−3589.2244	1.66728	−0.14980	1.67630	−0.15345
Kr	36	−5577.7193	3.13165	−0.29278	3.15621	−0.30272
Cd	48	−11186.6381	8.43566	−0.82064	8.55182	−0.86784
Xe	54	−14893.7970	12.66281	−1.24193	12.88098	−1.33080
Sm	62	−20858.7635	20.33356	−1.99349	20.78612	−2.17872
Yb	70	−28135.4602	30.78699	−2.99219	31.63882	−3.34297
W	74	−32312.6826	37.32466	−3.60309	38.46143	−4.07289
Hg	80	−39298.1672	49.00631	−4.66990	50.70659	−5.37678
Pb	82	−41827.9999	53.46107	−5.06815	55.39151	−5.87256
Rn	86	−47204.9084	63.29303	−5.93143	65.75845	−6.96351
Pu	94	−59315.6687	87.08065	−7.92786	90.94999	−9.56536
No	102	−73486.7522	117.51891	−10.31582	123.31854	−12.80277

of the generalized Gaunt interaction between electrons in subshells A and B, and in column 3 we list the retardation interaction $\overline{L}'^{\mathrm{ret}}_{AB}$. One sees that the dominant contribution to the Gaunt energy both for Ne and for Hg is the 1s-1s interaction. It should be mentioned that our evaluation of the 1s-1s Gaunt interaction for Hg ($2\overline{L}^{G}_{1s,1s} = +15.02$ Ry) agrees with the corresponding result quoted by Grant[4] [$-\frac{8}{3}F^{m}_{1}(1s,\ 1s) = +15.04$ Ry]. It is seen that, even though the K-electron interactions dominate the Gaunt energy shift, the neglect of the remaining contributions is by no means justified.

TABLE II. Average interaction energy between electron pairs for all subshells of Ne and for K shell of Hg. The Gaunt and retardation contributions are those referred to in Eq. (32). Both contributions are evaluated using the transverse interaction H'_{Br}. The orbital subscripts ± are used for $j = l \pm \frac{1}{2}$, respectively. Energies in Ry units.

Subshell		Gaunt	Retardation
Ne			
1s+	1s+	0.011 856 9	−0
	2s+	0.000 596 2	−0.000 059 7
	2p−	0.000 796 4	−0.000 125 7
	2p+	0.000 438 9	−0.000 125 2
2s+	2s+	0.000 069 6	−0
	2p−	0.000 057 4	−0.000 004 0
	2p+	0.000 067 9	−0.000 004 0
2p−	2p−	0.000 106 5	−0
	2p+	0.000 037 9	−0.000 000 0
2p+	2p+	0.000 105 7	−0
Hg			
1s+	1s+	7.507 796 2	−0
	2s+	0.830 069 9	−0.110 281 7
	2p−	1.612 099 2	−0.175 483 4
	2p+	0.599 938 7	−0.165 622 4
	3s+	0.181 319 0	−0.025 841 5
	3p−	0.329 321 4	−0.036 726 8
	3p+	0.131 736 5	−0.038 376 7
	3d−	0.008 620 6	−0.001 103 8
	3d+	0.003 595 7	−0.001 192 1
	4s+	0.044 996 2	−0.006 510 7
	4p−	0.077 597 6	−0.008 700 6
	4p+	0.031 284 8	−0.009 220 3
	4d−	0.002 216 1	−0.000 285 0
	4d+	0.000 920 3	−0.000 308 1
	4f−	0.000 005 5	−0.000 000 7
	4f+	0.000 002 2	−0.000 000 8
	5s+	0.008 599 1	−0.001 248 8
	5p−	0.013 010 0	−0.001 460 4
	5p+	0.005 004 5	−0.001 478 6
	5d−	0.000 219 6	−0.000 028 3
	5d+	0.000 086 2	−0.000 028 9
	6s+	0.000 727 5	−0.000 105 7

In DHF calculations a convenient technique for estimating binding energies is the "frozen-orbital" method in which atom-ion energy differences are evaluated by approximating ion orbitals with atom orbitals, i.e., by neglecting the effect of charge rearrangement on the ion orbitals. Koopmans's theorem[20] tells us that the resulting electrostatic binding is given by the DHF eigenvalue. The corresponding frozen-orbital approximation of the Breit contribution to binding energies is seen from Eq. (32) to be

$$\Delta\epsilon_A = \sum_{[B]\neq[A]} q_B\left(\overline{L}^{G}_{AB} + \overline{L}^{\mathrm{ret}}_{AB}\right) + (q_A - 1)\frac{2j_A + 1}{2j_A}\,\overline{L}^{G}_{AA}\,. \qquad (47)$$

The Gaunt and retardation contributions to the frozen-orbital energies are listed separately for all of the subshells of Hg in Table III. In column 2 of Table III we list the DHF eigenvalues. The Gaunt and retardation contributions evaluated using the transverse interaction are listed in the last two columns.

To include properly the effects of rearrangement on the binding energies it is of course necessary to evaluate separately the atom and ion energies and to identify the atom-ion energy difference with the electron binding energy. Contributions of the DHF and transverse interactions to the binding of K electrons in W, Hg, Pb, and Rn are listed in Table IV. Rearrangement effects on the transverse in-

TABLE III. Frozen-orbital contributions to electron binding energies for Hg ($Z = 80$). The Gaunt and retardation energies are evaluated using H'_{Br}. The electric energies are given by the DHF orbital eigenvalues. The entries give the respective contributions to one-electron binding energies assuming that rearrangement effects are negligible. Energies in Ry units.

Subshell		DHF	Gaunt	Retardation
(Hg)	1s+	−6148.6546	24.3548	−1.6064
	2s+	−1100.5281	3.4662	−0.3697
	2p−	−1053.7019	5.3248	−0.5107
	2p+	−910.3115	3.5144	−0.4902
	3s+	−266.2319	0.8127	−0.0976
	3p−	−245.2758	1.1892	−0.1257
	3p+	−213.0895	0.7887	−0.1158
	3d−	−178.8730	0.6990	−0.0875
	3d+	−172.0400	0.5628	−0.0850
	4s+	−61.2979	0.2137	−0.0285
	4p−	−52.2476	0.2935	−0.0342
	4p+	−44.3769	0.1907	−0.0302
	4d−	−29.5933	0.1492	−0.0206
	4d+	−28.1050	0.1185	−0.0199
	4f−	−8.9458	0.0650	−0.0090
	4f+	−8.6234	0.0527	−0.0088
	5s+	−10.2064	0.0424	−0.0058
	5p−	−7.0757	0.0501	−0.0060
	5p+	−5.6839	0.0308	−0.0050
	5d−	−1.3001	0.0142	−0.0020
	5d+	−1.1493	0.0106	−0.0019
	6s+	−0.6561	0.0036	−0.0005

TABLE IV. *K*-electron binding energies for various heavy elements. The electric, Gaunt, and retardation contributions are given by the atom-ion energy differences. Energies in Ry units.

Element	E_{DHF}	E'_G	E'_{ret}	E_{LS} [a]	E_{tot}	E_{expt} [b]
W	−32 312.683	37.325	−3.603			
$\mathrm{W}^+(1s^1)$	−27 176.698	19.311	−2.426			
Δ	−5 135.985	18.014	−1.177	8.65	−5110.50	−5110.46 ± 0.02
Hg	−39 298.167	49.006	−4.670			
$\mathrm{Hg}^+(1s^1)$	−33 156.521	25.678	−3.187			
Δ	−6 141.646	23.328	−1.483	11.28	−6108.52	−6108.39 ± 0.06
Pb	−41 828.000	53.461	−5.068			
$\mathrm{Pb}^+(1s^1)$	−35 323.199	28.122	−3.474			
Δ	−6 504.801	25.339	−1.594	12.27	−6468.79	−6468.67 ± 0.05
Rn	−47 204.908	63.293	−5.931			
$\mathrm{Rn}^+(1s^1)$	−39 929.538	33.536	−4.102			
Δ	−7 275.370	29.757	−1.829	14.43	−7233.01	−7233.08 ± 0.90

[a] Includes electron self-energy and vacuum polarization together with an estimated −0.08-Ry correlation energy (Ref. 21).

[b] Reference 23. Photoelectric work functions have been added to the published values.

teraction energies of Hg, determined by comparing the results of Tables III and IV, are seen to decrease the magnitudes of Gaunt and retardation energies by several percent.

To make comparison with experiment possible it is necessary to estimate the effect of the Lamb shift and of correlation on the *K*-electron binding energies. We take the Lamb-shift corrections from the recent calculation of Desiderio and Johnson[21] and use the empirical estimate of Cowan[22] for the correlation energy. Using the transverse interaction (rather than the Breit interaction used in Ref. 21), the discrepancy with experiment is reduced from about 0.1 to approximately 0.1 Ry.

In light of the existence of the precise electron-spectroscopy-for-chemical-analysis (ESCA) data currently available[23] for electron binding energies, it would be desirable to extend calculations of the type presented in Table IV throughout the Periodic Table.

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Light Shifts Due to Real Transitions in Optically Pumped Alkali Atoms*

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Light shifts and line narrowings due to real transitions in alkali atoms have been calculated for well-resolved $\Delta m = 0$, $\Delta F = 1$ transitions between ground-state sublevels. The shifts vary in a systematic way for the various $\Delta m = 1$ transitions. Resonant increases in the magnitude of the shift occur in the neighborhood of certain critical magnetic fields. The calculations are in excellent agreement with the recent experimental results of White, Hughes, Hayne, and Robinson.

I. INTRODUCTION

Optical-pumping experiments are often characterized by extremely narrow magnetic-resonance linewidths. For example, linewidths on the order of 1 Hz have been observed in alkali atoms. Because of these narrow linewidths, the transition frequencies of optically pumped vapors have been used as precise frequency standards[1,2] and for precision measurements of atomic parameters.[3,4] However, small shifts of these transition frequencies can be caused by many external factors, and such shifts can be an annoying experimental complication. Some of the more common sources of frequency shifts are the following: pressure shifts, which can be caused by collisions of the pumped atoms with other atoms or molecules[5]; wall shifts, which occur as a result of collisions of the pumped atoms with the container walls[6]; spin-exchange shifts, which occur as a result of the collisions of the pumped atoms with each other or with other pumped species[7,8]; Bloch-Siegert shifts, which are caused by nonresonant rf or microwave fields[9]; and light shifts, which are caused by the pumping light.[10]

The light shifts were first studied in detail by Barrat and Cohen-Tannoudji,[10] who recognized that shifts of two basic types occur. One type of light shift, which is referred to as the shift due to virtual transitions, is really just the mean Stark shift of the atomic sublevels in the oscillating electric field of the light wave.[11] Such shifts have been studied in some detail for the mercury isotopes,[12,13] for the alkali atoms,[5,14] and for metastable helium.[15] Shifts resulting from virtual transitions can be much larger than the magnetic-resonance linewidths.

A second type of light shift, referred to as the shift due to real transitions, is caused by the following mechanism: The absorption of a photon will transform a precessing ground-state atom to a precessing excited-state atom whose initial polarization at the instant of absorption is related to the ground-state polarization. The precession frequency of the excited atom will, in general, be greater than or less than the ground-state precession frequency. Consequently, when the polarized excited atom decays, a polarized ground-state atom will be generated, but the ground-state polarization will be rotated forward or backward with respect to the polarization of the atoms that did not absorb a photon. The net result of many such processes is a slight increase or decrease in the effective ground-state precession frequency.

This coherence carry-over has a second interesting consequence. Since the atoms return to the ground state with a nonrandom polarization, the net rate of destruction of ground-state polarization is decreased by the process of coherence carry-over. Thus, light shifts due to real transitions are accompanied by a narrowing of the magnetic-resonance lines. In contrast to the shifts due to virtual transitions, the shifts due to real transitions are always less than, or of the same order of magnitude as, the light-induced part of the magnetic-resonance linewidth.

The only detailed study of shifts due to real transitions has been made by Cohen-Tannoudji[16] for Hg^{199}. The agreement between theory and experiment was excellent, both for the shift and for the relaxation rates. Although light shifts are easily observed experimentally in many other systems besides Hg^{199}, no extensive comparisons between experiment and theory have been made. For high-spin Zeeman multiplets the theory is rather complicated, since many degenerate tran-