Relativistic and Magnetic Spin Interactions in Helium-Like Atoms*

J. SUCHER AND H. M. FOLEY
Columbia University, New York, New York
(Received May 7, 1954)

Relativistic and magnetic spin corrections to the ionization energy of He and O^{6+} are given. The magnetic spin interaction given by Sessler and Foley has been derived by a careful evaluation of the Breit operator. The relativistic corrections obtained by reduction of the Dirac equation differ from some previous expressions. With all known corrections taken into account, there remains a discrepancy with experiment of about 30 cm^{-1} in the case of He. Within the rather large experimental and theoretical uncertainties, there appears to be no residual discrepancy in the case of O^{6+}.

INTRODUCTION

CHANDRASEKHAR, Elbert, and Herzberg[1] have recently reviewed the agreement between the theoretical and experimental values of the ionization energy of He and the isoelectronic series to He. Sessler and Foley[2] have pointed out that a magnetic spin-spin interaction which does not vanish in a ^1S state must be included, and they have attempted an evaluation of the relativistic effects in He. There are several numerical errors in Ia and Ib. It is the purpose of the present paper (1) to give a quantum theoretical derivation of the magnetic spin interaction which was deduced on classical grounds in Ia, (2) to point out and correct certain errors in the previous treatments of the relativistic term, and (3) to give corrected and extended results for the magnetic and relativistic energies for He and O^{6+}.

In Sec. I it is shown that a consistent reduction of the two-electron Dirac equation leads unambiguously to the relativistic corrections to be applied to the Schrödinger nonrelativistic eigenvalue. Because of the singular potentials between the point charges in the problem there are certain pitfalls to be avoided. In Sec. II a careful working out of the expectation value of the "Breit operator" interaction between electrons is shown to include the magnetic spin-spin term given by Sessler and Foley (Ia). In Sec. III are given what are believed to be fairly accurate values for the energy terms for He and less accurate values for O^{6+}. It will be seen that a discrepancy of about 30 cm^{-1} remains in the case of He. Within the rather large theoretical and experimental uncertainties existing in the case of O^{6+}, however, there is no apparent discrepancy.

I. THE REDUCTION OF THE TWO-ELECTRON DIRAC EQUATION[3]

In the notation of Schiff,[4] the two-electron relativistic Hamiltonian is

$$H_D = -c(\boldsymbol{\alpha}_{\rm I}\cdot\mathbf{p}_{\rm I}+\boldsymbol{\alpha}_{\rm II}\cdot\mathbf{p}_{\rm II})-mc^2(\beta_{\rm I}+\beta_{\rm II})+U.$$

In the Dirac equation, $H_D\Psi=E\Psi$, we write the 16-component Ψ in the form

$$\Psi=\begin{pmatrix}\phi\\ \omega_1\\ \omega_2\\ \chi\end{pmatrix},$$

eliminate the "small" components ϕ, ω_1, ω_2, and obtain the "reduced" equation, correct to order α^2 $(\alpha=e^2/\hbar c)$:

$$H_R\chi=E\chi, \tag{1}$$

$$H_R=H_0+H_1+H_2, \tag{2}$$

with

$$H_0=\mathbf{p}_{\rm I}^2/2m+\mathbf{p}_{\rm II}^2/2m+U, \tag{3}$$

$$H_1=-\frac{1}{4m^2c^2}\left[\mathbf{p}_{\rm I}\cdot f\mathbf{p}_{\rm I}+\mathbf{p}_{\rm II}\cdot f\mathbf{p}_{\rm II}-\frac{\mathbf{p}_{\rm I}^2\mathbf{p}_{\rm II}^2}{m}\right],\quad f=E-U, \tag{4}$$

$$H_2=\frac{e\hbar}{4m^2c^2}[\boldsymbol{\sigma}_{\rm I}\cdot(\mathbf{E}_{\rm I}\times\mathbf{p}_{\rm I})+\boldsymbol{\sigma}_{\rm II}\cdot(\mathbf{E}_{\rm II}\times\mathbf{p}_{\rm II})],\quad \mathbf{E}_{\rm I}=\boldsymbol{\nabla}_{\rm I}(U/e). \tag{5}$$

The nonrelativistic equation,

$$H_0\psi=E_0\psi, \tag{6}$$

is imagined to have been solved to a high accuracy and the expectation values of H_1 and H_2 are to be evaluated with the resulting ψ function.

The spin-orbit energy H_2 vanishes in the ground state of helium-like atoms.

We expand (4) with the aid of the equation

$$\mathbf{p}_{\rm I}\cdot f\mathbf{p}_{\rm I}=f\mathbf{p}_{\rm I}^2+\langle\mathbf{p}_{\rm I}f\rangle\cdot\mathbf{p}_{\rm I},$$

in which the angular bracket indicates that the differential operator $\mathbf{p}_{\rm I}$ acts only on the f function within the bracket. Thus the expectation value of H_1 becomes

$$E_1=E_1'+\epsilon, \tag{7}$$

$$E_1'=-\frac{1}{8m^3c^2}[(\mathbf{p}_{\rm I}^2\psi,\mathbf{p}_{\rm I}^2\psi)+(\mathbf{p}_{\rm II}^2\psi,\mathbf{p}_{\rm II}^2\psi)], \tag{8a}$$

$$\epsilon=-\frac{1}{4m^2c^2}[(\psi,\langle\mathbf{p}_{\rm I}f\rangle\cdot\mathbf{p}_{\rm I}\psi)+(\psi,\langle\mathbf{p}_{\rm II}f\rangle\cdot\mathbf{p}_{\rm II}\psi)], \tag{9}$$

* Supported by the National Science Foundation.
[1] Chandrasekhar, Elbert, and Herzberg, Phys. Rev. **91**, 1172 (1953).
[2] A. M. Sessler and H. M. Foley, Phys. Rev. **92**, 1321 (1953), and Phys. Rev. **92**, 1321–1322 (1953); hereafter referred to as Ia and Ib respectively.
[3] G. Breit, Phys. Rev. **34**, 553 (1929); Phys. Rev. **39**, 616 (1932).
[4] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 311.

in which the relations

$$[(\mathbf{p}_{\rm I}^2+\mathbf{p}_{\rm II}^2)/2m]\psi=f\psi,$$

$$(\psi,f(\mathbf{p}_{\rm I}^2+\mathbf{p}_{\rm II}^2)\psi)=\frac{1}{2m}((\mathbf{p}_{\rm I}^2+\mathbf{p}_{\rm II}^2)\psi,(\mathbf{p}_{\rm I}^2+\mathbf{p}_{\rm II}^2)\psi),$$

$$(\mathbf{p}_{\rm I}^2\psi,\mathbf{p}_{\rm II}^2\psi)=(\psi,\mathbf{p}_{\rm I}^2\cdot\mathbf{p}_{\rm II}^2\psi),$$

have been used. Now for potential functions which are everywhere bounded $\mathbf{p}_{\rm I}^2\psi$ is well behaved and the usual Hermitean property of the operator $\mathbf{p}_{\rm I}$ enables one to transform E_1' as

$$E_1'\rightarrow-\frac{1}{8m^3c^2}[(\psi,\mathbf{p}_{\rm I}^4\psi)+(\psi,\mathbf{p}_{\rm II}^4\psi)]. \quad (8b)$$

For the singular potentials corresponding to point particles, however, this transformation cannot be performed; in fact, the two forms of E_1' in Eq. (8) differ by finite terms which have the form of delta functions at the singular points. This can be seen clearly by evaluating the two forms of (8) for an extended nuclear charge distribution and considering the limiting values for point charges. [See Eq. (19).] In his *Handbuch* article[5] Bethe has given E_1' in the form (8b), but the evaluation of this energy term was actually carried out with the correct form (8a).

The term ϵ in E_1 may be written, after an integration by parts, as

$$\epsilon=E_1''+E_1'''=(\psi,H_1''\psi)+(\psi,H_1'''\psi), \quad (9)$$

$$H_1''=2\pi\mu_0^2Z[\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)], \quad (10)$$

$$H_1'''=-4\pi\mu_0^2\delta(\mathbf{r}_{12}). \quad (11)$$

Eriksson[6] has evaluated H_1 [Eq. (4)] by an expansion in which the singular terms $\Delta_{\rm I}U$ and $\Delta_{\rm II}U$ have been dropped. (See the last equation on p. 764 of reference 6.) It is clear that a finite energy contribution has thus been neglected.

II. BREIT INTERACTION

The magnetic and retarded electrostatic interaction between electrons, to order α^2, has been given by Breit[3] as

$$B=\frac{-e^2}{2r_{12}}[\boldsymbol{\alpha}_{\rm I}\cdot\boldsymbol{\alpha}_{\rm II}+(\boldsymbol{\alpha}_{\rm I}\cdot\mathbf{n})(\boldsymbol{\alpha}_{\rm II}\cdot\mathbf{n})]. \quad (12)$$

The expectation value of B has been shown by Breit to be

$$E_3=\frac{-e^2}{8m^2c^2}[(\chi,M\xi_{\rm I}\xi_{\rm II}\chi)+(\xi_{\rm I}\chi,M\xi_{\rm II}\chi)+(\xi_{\rm II}\chi,M\xi_{\rm I}\chi)+(\xi_{\rm I}\xi_{\rm II}\chi,M\chi)] \quad (13)$$

where χ is defined by Eq. (1) and

$$\xi_{\rm I}\equiv\boldsymbol{\sigma}_{\rm I}\cdot\mathbf{p}_{\rm I},\quad \xi_{\rm II}\equiv\boldsymbol{\sigma}_{\rm II}\cdot\mathbf{p}_{\rm II},$$
$$M\equiv\frac{1}{r_{12}}[\boldsymbol{\sigma}_{\rm I}\cdot\boldsymbol{\sigma}_{\rm II}+(\boldsymbol{\sigma}_{\rm I}\cdot\mathbf{n})(\boldsymbol{\sigma}_{\rm II}\cdot\mathbf{n})]. \quad (13')$$

It is desirable to express E_3 as the expectation value of an operator H_3 which is applied to the Schrödinger-Pauli function χ. It is easily seen that one may write

$$(\xi_{\rm I}\chi,M\xi_{\rm II}\chi)=(\chi,\xi_{\rm I}M\xi_{\rm II}\chi),$$
$$(\xi_{\rm II}\chi,M\xi_{\rm I}\chi)=(\chi,\xi_{\rm II}M\xi_{\rm I}\chi) \quad (14)$$

by an integration by parts. When we consider, however, the last term in Eq. (13) we have

$$(\xi_{\rm I}\xi_{\rm II}\chi,M\chi)=(\xi_{\rm II}\chi,\xi_{\rm I}M\chi)\neq(\chi,\xi_{\rm II}\xi_{\rm I}M\chi),$$

since the function $\xi_{\rm I}M\chi$ varies as $1/r_{12}^2$, so that a second integration by parts leads to a nonvanishing "surface" term. The evaluation of this term is carried out in the Appendix. The result is

$$(\xi_{\rm I}\xi_{\rm II}\chi,M\chi)=(\chi,\xi_{\rm II}\xi_{\rm I}M\chi)+(16\pi/3)\hbar^2(\chi,\boldsymbol{\sigma}_{\rm I}\cdot\boldsymbol{\sigma}_{\rm II}\delta(\mathbf{r}_{12})\chi). \quad (15)$$

We combine these results and write

$$E_3=(\chi,H_3\chi)=E_3'+E_3''=(\chi,H_3'\chi)+(\chi,H_3'\chi), \quad (16)$$

$$H_3'=\frac{-e^2}{8m^2c^2}[M\xi_{\rm I}\xi_{\rm II}+\xi_{\rm I}M\xi_{\rm II}+\xi_{\rm II}M\xi_{\rm I}+\xi_{\rm I}\xi_{\rm II}M], \quad (17)$$

$$H_3''=-(8\pi/3)\mu_0^2\boldsymbol{\sigma}_{\rm I}\cdot\boldsymbol{\sigma}_{\rm II}\delta(\mathbf{r}_{12}). \quad (18)$$

H_3' was obtained and reduced by Breit;[3] the additional operator H_3'' is just the quantum theoretical form of the magnetic spin-spin interaction given by Sessler and Foley (Ia).[7]

Our results appear to differ from those of Chraplyvy,[8] who employed a Foldy-Wouthuysen transformation on this same problem.

III. THE IONIZATION ENERGIES OF He AND O^{6+}

A. He

The corrections E_1', E_1'', E_1''', and E_3'' to the nonrelativistic energy E_0 have been calculated with the Hylleraas three-parameter function;[9] the results are given in Table I, together with those from a Hartree wave function and a Hydrogenic function.

We have examined the accuracy of these results by repeating the calculations for E_1'', E_1'', and E_3'' $(=-2E_1''')$ with the Hylleraas six-parameter function,[9]

[5] H. A. Bethe, *Handbuch der Physik* (Springer, Berlin, 1933), Vol. 24, II, p. 384.

[6] H. A. S. Eriksson, Z. Physik **109**, 762 (1938).

[7] Since the completion of this paper it has come to our attention that this result was derived by V. Berestetskii and L. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **19**, 673 (1949) by the same procedure that we have employed.

[8] Z. V. Chraplyvy, Phys. Rev. **91**, 388 (1953).

[9] E. A. Hylleraas, Z. Physik **54**, 347 (1929).

TABLE I. The relativistic and magnetic spin corrections in $\alpha^2 Ry$, with various wave functions.

	He Present calc	He Hartree	He Hydrogenic	O^{6+} Present calc
$-E_1'$	26.71	26.23[a]	20.30[b]	9174.6
$-E_1''$	−22.60	−22.60[a]	−19.20[b]	−7492.0
$-E_1'''$	0.73	1.18	1.20	101.5
$-E_3''$	−1.46	−2.36	−2.40	−203.0
E_{ion}	−4.00			−1024.0
$\Sigma(\alpha^2 Ry)$	−0.62			557.1
$\Sigma(\text{cm}^{-1})$	−3.62			3255.7

[a] See reference 2.
[b] See reference 5.

giving, in units of $\alpha^2 \times Ry$: $E_1''=22.83$, $E_1'''=0.70$, and with the ten-parameter variational function, obtained by Chandrasekhar, Elbert, and Herzberg,[10] giving: $E_1''=22.74$, $E_1'''=0.69$. The close agreement between these values and those obtained with the three-parameter function leads us to believe that our results are accurate to within one or two wave numbers.

Most of the labor in the calculation of E_1' was avoided by using the equation

$$(\mathbf{p}_1^2\psi,\mathbf{p}_1^2\psi)=(\psi,\mathbf{p}_1^4\psi)-4\pi\int\left\{\left(\frac{\partial\psi^2}{\partial r_1}\right)_{r_1=0}+\left(\frac{\partial\psi^2}{\partial r_{12}}\right)_{r_{12}=0}\right\}d\mathbf{r}_2. \quad (19)$$

The term $(\psi,\mathbf{p}_1^4\psi)$ has been calculated previously by Eriksson.[6]

The agreement between the values obtained for E_1' and E_1'' with Hylleraas and Hartree functions is satisfactory. The difference in values of E_1''' (and E_3'') is ascribed to the absence of correlation in the Hartree function. There can be little doubt that the Hylleraas results are more reliable.

The value of E_3'' from the Hylleraas function given in Ia is in error because of an incorrect normalization of the wave function. The operator expression for E_1''' given in Ib is in error by a factor of two. Consequently the remark that the calculation of this quantity by Bethe is incorrect was not justified.

TABLE II. The theoretical and experimental values of the ionization energies of He and O^{6+}, in cm^{-1}.

Atom	$(\text{I.E.})_{\text{nonrel}}$	$+\Sigma$	$-E_3'$	Mass pol.	$(\text{I.E.})_{\text{theor}}$	$(\text{I.E.})_{\text{exp}}$
He	198 290.7[a]	−3.62	0.88[b]	−5[c]	198 283	198 313±5[a]
O^{6+}	5 959 898[a]	3256	53[b]	2[c]	5 963 209	5 963 000±600[a]

[a] See reference 1.
[b] See reference 6.
[c] See reference 11.

[10] Chandrasekhar, Elbert, and Herzberg (see reference 1); the normalization constant given there should be 1.359625 [G. Herzberg (private communication)].

B. O^{6+}

Inasmuch as the various relativistic, magnetic, and Lamb shift terms vary as Z^4 and Z^3, whereas the nonrelativistic eigenvalue varies only as Z^2, it is of interest to examine the case of O^{6+}. The calculations were made with the wave function obtained by Eriksson[6] by an expansion in inverse powers of Z. The results are given in Table I. The accuracy of the nonrelativistic eigenvalue, and of the quantities given for O^{6+} in the table is uncertain.

C. Ionization Potentials of He and O^{6+}

In Table I, E_{ion} denotes the relativistic correction for He^{1+} and O^{7+}. The quantity $\sum$ gives the correction to the ionization energy from the terms evaluated above. In Table II these quantities and the additional small terms, E_3' evaluated by Eriksson[6] and the "mass polarization" term from Robinson,[11] are added to the nonrelativistic ionization energies to give $(\text{I.E.})_{\text{theor}}$.†

It is seen that a difference between this theoretical result and experiment of about 30 cm^{-1} exists in the case of He. The Lamb shift would add about 1 cm^{-1} to this quantity, as estimated by Hakansson.[12] (The Hylleraas "eighth approximation" calculation of the nonrelativistic eigenvalue, which is presumably less reliable[1] than the strictly variational result employed in Table II, would give an almost exact agreement between theory and experiment.) Presumably the discrepancy may be accounted for by the inaccuracy in the nonrelativistic energy calculated from the Hylleraas wave function. The corresponding difference in the case of O^{6+} is about −200 cm^{-1} to which the Lamb shift would add about 400 cm^{-1},[12] giving about +200 cm^{-1} for the remaining discrepancy. This is well within the rather large experimental uncertainty.‡

We wish to acknowledge a profitable discussion with Dr. A. M. Sessler.

APPENDIX

We have

$$(\xi_{\text{II}}\chi,\xi_{\text{I}}M\chi)=\int\int(\xi_{\text{II}}\chi)^\dagger(\xi_{\text{I}}M\chi)d\mathbf{r}_1d\mathbf{r}_2, \quad (1)$$

the symbols being defined in Eq. (13′). We may write

$$(\xi_{\text{II}}\chi)^\dagger(\xi_{\text{I}}M\chi)=\chi^\dagger\xi_{\text{II}}\xi_{\text{I}}M\chi-\mathbf{p}_{\text{II}}\cdot(\chi^\dagger\boldsymbol{\sigma}_{\text{II}}\xi_{\text{I}}M\chi),$$

[11] H. A. Robinson, Phys. Rev. **51**, 14 (1937).
† *Note added in proof.*—The value of E_3' taken from Ericksson does not agree with Ericksson's formula (p. 771 of reference 6), but should be increased by a factor 2 to 1.76 cm^{-1}. This result was obtained independently by R. P. Feynman and M. Baranger (private communication).
[12] H. E. V. Hakansson, Arkiv. Fysik **1**, 555 (1950).
‡ *Note added in proof.*—Professor G. Herzberg has kindly communicated to us the result of a 10-term variational calculation of the nonrelativistic ionization energy of 0^{6+}. His result increases $(IE)_{\text{nonrel}}$ by only 40 cm^{-1}. This removes the principal uncertainty in the calculation and thus confirms the general agreement of theory and experiment for 0^{6+}.

whence

$$(\xi_{II}\chi,\xi_I M\chi,)=(\chi\xi_{II}\xi_I M\chi)+J,$$

$$J=-\int\int \mathbf{p}_{II}\cdot(\chi^\dagger\boldsymbol{\sigma}_{II}\xi_I M\chi)d\mathbf{r}_1 d\mathbf{r}_2. \qquad (2)$$

Let S_a be a sphere of radius a about the point $\mathbf{r}_1$. Then, by Gauss' theorem, we have

$$J=\hbar^2\int I(\mathbf{r}_1)d\mathbf{r}_1,$$

$$I(\mathbf{r}_1)=\lim_{a\to 0} I_a, \qquad (3)$$

$$I_a=-\int_{S_a}(\chi^\dagger\boldsymbol{\sigma}_{II}(\boldsymbol{\sigma}_I\cdot\nabla_I M\chi))\cdot\mathbf{n}dS_a,$$

where $\mathbf{n}$ is the outward normal on S_a. I_a may be rewritten, on carrying out the differentiation,

$$I_a=-[I_a'+I_a''],$$

$$I_a'=\int_{S_a}\chi^\dagger Q\chi d\Omega,\quad I_a''=\int_{S_a}\chi^\dagger P\chi d\Omega,$$

$$Q=r_{12}^2(\boldsymbol{\sigma}_{II}\cdot\mathbf{n})(\boldsymbol{\sigma}_I\cdot\langle\nabla_I M\rangle), \qquad (4)$$

$$P=r_{12}^2(\boldsymbol{\sigma}_{II}\cdot\mathbf{n})\boldsymbol{\sigma}_I\cdot M\nabla_I.$$

Since $M\sim 1/r_{12}$, $\lim_{a\to 0}P=0$, whence

$$\lim_{a\to 0} I_a''=0, \qquad (5)$$

if χ is regular at $\mathbf{r}_1=\mathbf{r}_2$, as is assumed. Carrying out the differentiation of M, we get

$$\boldsymbol{\sigma}_I\cdot\nabla_I M=\frac{1}{r_{12}^2}\boldsymbol{\sigma}_I\cdot\{[\boldsymbol{\sigma}_I\cdot\boldsymbol{\sigma}_{II}+(\boldsymbol{\sigma}_I\cdot\mathbf{n})(\boldsymbol{\sigma}_{II}\cdot\mathbf{n})]\mathbf{n}+(\boldsymbol{\sigma}_I\cdot\mathbf{n})[(\boldsymbol{\sigma}_{II}\cdot\mathbf{n})\mathbf{n}-\boldsymbol{\sigma}_{II}]+(\boldsymbol{\sigma}_{II}\cdot\mathbf{n})[(\boldsymbol{\sigma}_I\cdot\mathbf{n})\mathbf{n}-\boldsymbol{\sigma}_I]\}$$

$$=\frac{2i}{r_{12}^2}\boldsymbol{\sigma}_{II}\cdot[\boldsymbol{\sigma}_I\times\mathbf{n}]$$

on repeated use of the formula,

$$(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{B})=\mathbf{A}\cdot\mathbf{B}+i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{B}),$$

for arbitrary vectors $\mathbf{A}$ and $\mathbf{B}$. Hence we find

$$Q=2i(\boldsymbol{\sigma}_{II}\cdot\mathbf{n})(\boldsymbol{\sigma}_{II}\cdot[\boldsymbol{\sigma}_I\times\mathbf{n}])=-2[\boldsymbol{\sigma}_I\cdot\boldsymbol{\sigma}_{II}-(\boldsymbol{\sigma}_I\cdot\mathbf{n})(\boldsymbol{\sigma}_{II}\cdot\mathbf{n})].$$

Then

$$\int_{S_a}Qd\Omega=-2\sum_{i,j}\sigma_{Ii}\sigma_{IIj}\left(4\pi\delta_{ij}-\frac{4\pi}{3}\delta_{ij}\right)=-\frac{16\pi}{3}\boldsymbol{\sigma}_I\cdot\boldsymbol{\sigma}_{II},$$

and, as follows quite rigorously for continuous χ,

$$\lim_{a\to 0} I_a'=-\frac{16\pi}{3}[\chi^\dagger\boldsymbol{\sigma}_I\cdot\boldsymbol{\sigma}_{II}\chi]_{a=0}. \qquad (6)$$

Combining (3), (4), (5), and (6) we get

$$J=\frac{16\pi}{3}\hbar^2\int[\chi^\dagger\boldsymbol{\sigma}_I\cdot\boldsymbol{\sigma}_{II}\chi]_{\mathbf{r}_1=\mathbf{r}_2}d\mathbf{r}_1$$

$$=(16\pi/3)\hbar^2(\chi,\boldsymbol{\sigma}_I\cdot\boldsymbol{\sigma}_{II}\delta(\mathbf{r}_{12})\chi),$$

where $\delta(\mathbf{r}_{12})$ is the Dirac delta function between the two two electrons. This yields Eq. (15) if we recall Eq. (2) which defines J.