

screened potential were calculated and compared with the result of exact phase-shift calculations,  $R_{\text{ex}}$ . Table III lists these results in detail and permits the recognition of the following:

(1) The Molière approximation renders  $R$  by Eqs. (15) and (16) with an error of the order  $\xi$  [Eq. (5) and Table I].

(2) The classical approximation renders  $R_{\text{class}}$  by Eqs. (22) and (23) with an error which is comparable to that of  $R$  for scattering angles larger than  $10^\circ$ .

(3) The large-angle approximation renders  $R_{\text{L.A.}}$  by Eqs. (25) and (26) with errors generally larger than of  $R_{\text{class}}$ .

(4) The first-order Born approximation gives values,  $R_{\text{Born}}$ , the errors of which exceed those of all the other approximations. Even for the light element  $Z=29$  and for small angles the errors are larger than 10%.

#### ACKNOWLEDGMENTS

We are indebted to J. W. Motz for numerous discussions and for pointing out to us the need for rather simple and yet sufficiently accurate calculations of the elastic electron-scattering cross section.

We would also like to acknowledge the valuable assistance of R. L. Scott in preparing the program and performing the computations.

## Analytical Relativistic Self-Consistent Field Theory\*

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(Received 25 March 1964)

The analytical self-consistent field (SCF) theory, based on the relativistic Breit equation generalized for many particles, was developed for closed-shell systems. The relativistic SCF equations, both of the absolute and of the expansion method type, were derived in the four-component spinor representation. The Breit operator was considered in the first-order perturbation theory. The formulas for the relativistic atomic integrals were derived in terms of simple functions.

### INTRODUCTION

IN this work the relativistic Breit equation<sup>1</sup> is considered generalized for many-particle systems. Then the relativistic self-consistent field (SCF) theory for closed-shell systems is developed, partially using an analogy with the expansion method<sup>2,3</sup> of the nonrelativistic theory. The applications<sup>4</sup> of the expansion method encourage such an attempt at a relativistic extension.

While this work was outlined,<sup>5</sup> an approach related to the numerical SCF method appeared in the literature.<sup>6</sup> Recently, another approach was made.<sup>7</sup>

\* The work was originated at the University of Chicago, Chicago, Illinois.

<sup>1</sup> H. A. Bethe and E. E. Salpeter, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXXV, Sec. 38.

<sup>2</sup> C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).

<sup>3</sup> C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960).

<sup>4</sup> For further references see, e.g., M. Synek, *Phys. Rev.* **131**, 1572 (1963); **133**, A961 (1964); C. C. J. Roothaan and M. Synek, *ibid.* **133**, A1263 (1964).

<sup>5</sup> A brief notice (by M. Synek) appeared in a circular, Division of Physical Sciences, The University of Chicago, 1961, p. 25 (unpublished). A version of the presented work was deposited as a Research Report No. SY1, Department of Physics, DePaul University, Chicago, Illinois, 1963 (unpublished). See also M. Synek, *Bull. Am. Phys. Soc.* **9**, 563 (1964).

<sup>6</sup> I. P. Grant, *Proc. Roy. Soc. (London)* **A262**, 555 (1961).

<sup>7</sup> G. L. Malli and C. C. J. Roothaan, *Bull. Am. Phys. Soc.* **9**, 101 (1964).

### GENERAL CONSIDERATIONS

The validity of the Breit equation for two electrons has been proved both theoretically<sup>1</sup> and by practical applications.<sup>8</sup> It is quite plausible to assume that even in a many-electron system mutual interactions between electrons can be approximated by interactions within all possible pairs of electrons where in every pair only the two-electron Breit interaction is considered. Similar although simpler consideration was performed already by Swirls<sup>9</sup> in an atomic case, by going from the Dirac equation to the approximate many-electron relativistic equation (while omitting the Breit operator). In the molecular case the influence of nuclei can be approximated as an external field.<sup>10</sup>

Hence we introduce the generalized Breit equation for a system of  $N$  electrons (and  $M$  nuclei) as follows:

$$\left( E - \sum_{\mu=1}^N H^{\mu} - \frac{1}{2} e^2 \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^N \frac{1}{r^{\mu\nu}} \right) U \\ = -\frac{1}{4} e^2 \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^N \frac{1}{r^{\mu\nu}} \left[ \alpha^{\mu} \cdot \alpha^{\nu} + \frac{(\alpha^{\mu} \cdot \mathbf{r}^{\mu\nu})(\alpha^{\nu} \cdot \mathbf{r}^{\mu\nu})}{(r^{\mu\nu})^2} \right] U, \quad (1)$$

<sup>8</sup> G. Araki, *Proc. Phys. Math. Soc. Japan* **19**, 128 (1937).

<sup>9</sup> B. Swirls, *Proc. Roy. Soc. (London)* **A152**, 625 (1935).

<sup>10</sup> K. S. Viswanathan, *Proc. Indian Acad. Sci., Sec. A* **50**, No. 1 (1959). Diatomic molecules are considered.

where

$$H^\mu = -e\varphi(\mathbf{r}^\mu) + \beta^\mu mc^2 + \boldsymbol{\alpha}^\mu \cdot [c\mathbf{p}^\mu + e\mathbf{A}(\mathbf{r}^\mu)].$$

Here the notation introduced earlier<sup>2</sup> is applied as widely as possible.  $E$  is the "electronic" energy of a system. The wave function  $U$  depends on the positions  $r^1, r^2, \dots, r^N$  of the  $N$  electrons and has  $4^N$  spinor components. The operator  $H^\mu$  is the Dirac Hamiltonian (considered here for  $M$  nuclei). Dirac matrices  $\boldsymbol{\alpha}^\mu$  and  $\beta^\mu$  operate on the spinor components of  $U$  (for the  $\mu$ th electron) in the usual way. The momentum operator  $\mathbf{p}^\mu$  is, of course, given by  $-i\hbar \text{grad}^\mu$ .  $\varphi(\mathbf{r}^\mu)$  and  $\mathbf{A}(\mathbf{r}^\mu)$  are the scalar and vector potentials of an "external" electromagnetic field (including the potentials of all nuclei).  $\mathbf{r}^{\mu\nu}$  is the distance between the  $\mu$ th and  $\nu$ th electrons. The operator on the right-hand side of the generalized Breit equation (1) will be called the generalized Breit operator and denoted by  $B$ . If we neglect the operator  $B$  we obtain the zeroth approximation expressed by the equation

$$\left( \sum_{\mu=1}^N H^\mu + \frac{1}{2}e^2 \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^N \frac{1}{r^{\mu\nu}} \right) U_0 = E_0 U_0, \quad (2)$$

which will be called the generalized Swirls<sup>9</sup> equation (scalar and vector potentials of an "external" field including the potentials of all nuclei are now included). Equation (2) can also be written as

$$\mathcal{H}_0 U_0 = E_0 U_0, \quad (2')$$

where the quantities  $\mathcal{H}_0$ ,  $E_0$ , and  $U_0$  are the zeroth-approximation Hamiltonian, "electronic" energy, and wave function (with  $4^N$  spinor components), respectively.

The goal of this treatment is to find a relativistic analogy to the SCF expansion method for the solution of Eq. (2) and, using an obtained approximation to the wave function  $U_0$ , to find the correction due to the generalized Breit operator  $B$  by the first-order<sup>11</sup> perturbation theory.

Let us introduce the  $\kappa$ th relativistic (atomic or molecular) orbital spinor for the  $\mu$ th electron as follows:

$$\Psi_{\kappa}^{\mu} \equiv \begin{pmatrix} \psi_{\kappa 1}^{\mu} \\ \psi_{\kappa 2}^{\mu} \\ \psi_{\kappa 3}^{\mu} \\ \psi_{\kappa 4}^{\mu} \end{pmatrix}; \quad (3)$$

the  $\rho$ th component of this spinor is

$$\psi_{\kappa \rho}^{\mu} \equiv \psi_{\kappa \rho}^{\mu}(x^{\mu}, y^{\mu}, z^{\mu}); \quad \rho = 1, 2, 3, 4.$$

Now let us consider a closed-shell ground state. We know that in the nonrelativistic SCF the wave function

<sup>11</sup> The reason for using the *first*-order perturbation theory is based on the discussion given in Ref. 1, following Eq. (38.7). (This discussion does not find it correct to use a higher order perturbation for treating the Breit operator.) Otherwise it would not be difficult to associate Breit operators with Coulombic electron-repulsion terms and to treat both on the same footing by an SCF treatment; in case of the analytical atomic SCF treatment the same integrals would be used as calculated at the end of this article.

is represented by one antisymmetrized product. In the relativistic SCF we expect that the wave function will consist of  $4^N$  components where each component will be a certain antisymmetrized product:

$$U_0 \approx \Phi \equiv \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_{4^N} \end{pmatrix}; \quad \phi_{\omega} \equiv (N!)^{-1/2} \begin{vmatrix} \psi_{1\rho_1}^1 \psi_{2\rho_2}^1 \cdots \psi_{N\rho_N}^1 \\ \psi_{1\rho_1}^2 \psi_{2\rho_2}^2 \cdots \psi_{N\rho_N}^2 \\ \vdots \\ \psi_{1\rho_1}^N \psi_{2\rho_2}^N \cdots \psi_{N\rho_N}^N \end{vmatrix}; \quad (4)$$

$$\omega = 1, 2, \dots, 4^N.$$

Components of  $\Phi$  are built by letting  $\rho_1, \rho_2, \dots, \rho_N$  be equal to 1, 2, 3, 4 for every  $\rho_k$  independently. Obviously, the spinor  $\Phi$  could also be built by using  $\psi^{\mu}_{\kappa\rho}$  instead of  $\psi_{\kappa\rho}^{\mu}$  (cf. Swirls<sup>9</sup>); then the components of  $\Phi$  would only be arranged in a different order. It is easy to see that the spinor  $\Phi$  can also be written as

$$\Phi = (N!)^{-1/2} \begin{vmatrix} \Psi_1^1 \Psi_2^1 \cdots \Psi_N^1 \\ \Psi_1^2 \Psi_2^2 \cdots \Psi_N^2 \\ \vdots \\ \Psi_1^N \Psi_2^N \cdots \Psi_N^N \end{vmatrix}, \quad (5)$$

where the determinant is defined in the usual way except that the product of two spinors is here always defined as if it were a direct product of two vectors; e.g.,

$$\Psi_{\kappa}^{\mu} \Psi_{\lambda}^{\nu} \equiv \begin{pmatrix} \psi_{\kappa 1}^{\mu} \\ \psi_{\kappa 2}^{\mu} \\ \psi_{\kappa 3}^{\mu} \\ \psi_{\kappa 4}^{\mu} \end{pmatrix} \times \begin{pmatrix} \psi_{\lambda 1}^{\nu} \\ \psi_{\lambda 2}^{\nu} \\ \psi_{\lambda 3}^{\nu} \\ \psi_{\lambda 4}^{\nu} \end{pmatrix} \equiv \begin{pmatrix} \psi_{\kappa 1}^{\mu} \psi_{\lambda 1}^{\nu} \\ \psi_{\kappa 1}^{\mu} \psi_{\lambda 2}^{\nu} \\ \psi_{\kappa 1}^{\mu} \psi_{\lambda 3}^{\nu} \\ \psi_{\kappa 1}^{\mu} \psi_{\lambda 4}^{\nu} \\ \psi_{\kappa 2}^{\mu} \psi_{\lambda 1}^{\nu} \\ \vdots \\ \psi_{\kappa 4}^{\mu} \psi_{\lambda 4}^{\nu} \end{pmatrix}. \quad (6)$$

The form (5) of the spinor  $\Phi$  can also be considered as a plausible analogy to the nonrelativistic antisymmetrized product.

Clearly, the spinor  $\Psi_{\kappa}^{\mu}$  can now be treated in many respects in the same way as the nonrelativistic molecular spin orbital<sup>2</sup> and a number of analogous statements could be proved.

Now we assume that

$$\int \Psi_{\kappa}^* \Psi_{\lambda} dv = \delta_{\kappa\lambda}, \quad (7)$$

where  $dv$  is the one-electron volume element and

$$\Psi_{\kappa}^* \equiv (\bar{\psi}_{\kappa 1} \bar{\psi}_{\kappa 2} \bar{\psi}_{\kappa 3} \bar{\psi}_{\kappa 4}), \quad (8)$$

$\bar{\psi}_{\kappa\rho}$  being the complex conjugate of  $\psi_{\kappa\rho}$ ;  $\rho = 1, 2, 3, 4$  (barred quantities will always be understood as complex conjugates); the integrand in (7) is simply evaluated as if it were a scalar product of two vectors. Equation (7) implies

$$\int \Phi^* \Phi dv = 1; \quad (9)$$

$$E_0 = \int U_0^* \mathcal{H}_0 U_0 dv \approx \int \Phi^* \mathcal{H}_0 \Phi dv \equiv E_{00}. \quad (10)$$

It is easy to see that

$$E_{00} = \sum_{\kappa=1}^N H_{\kappa} + \frac{1}{2} \sum_{\kappa, \lambda=1}^N (J_{\kappa\lambda} - K_{\kappa\lambda}), \quad (11)$$

where

$$H_{\kappa} = \bar{H}_{\kappa} = \int \Psi_{\kappa}^* H \Psi_{\kappa} dv, \quad (12)$$

$$J_{\kappa\lambda} = J_{\lambda\kappa} = \bar{J}_{\kappa\lambda} = \bar{J}_{\lambda\kappa} = e^2 \int \Psi_{\kappa}^{\mu*} \Psi_{\lambda}^{\nu*} \frac{1}{r^{\mu\nu}} \Psi_{\kappa}^{\mu} \Psi_{\lambda}^{\nu} dv^{\mu\nu}, \quad (13)$$

$$K_{\kappa\lambda} = K_{\lambda\kappa} = \bar{K}_{\kappa\lambda} = \bar{K}_{\lambda\kappa} = e^2 \int \Psi_{\kappa}^{\mu*} \Psi_{\lambda}^{\nu*} \frac{1}{r^{\mu\nu}} \Psi_{\lambda}^{\mu} \Psi_{\kappa}^{\nu} dv^{\mu\nu}; \quad (14)$$

clearly

$$J_{\kappa\kappa} = K_{\kappa\kappa}. \quad (15)$$

#### THE ABSOLUTE (HARTREE-FOCK) RELATIVISTIC SCF EQUATIONS FOR A CLOSED-SHELL GROUND STATE

Applying the variational treatment to the Eq. (11) it is easy to derive the absolute SCF equations

$$F \Psi_{\kappa} = \epsilon_{\kappa} \Psi_{\kappa}; \quad \kappa = 1, 2, \dots, N; \quad (16)$$

where

$$F = H + G, \quad G = \sum_{\kappa} (J_{\kappa} - K_{\kappa}); \quad (17)$$

( $H$  is the Dirac Hamiltonian which could generally be considered for  $M$  nuclei);  $J_{\kappa}$  and  $K_{\kappa}$  are, of course, the Coulomb and exchange operators forming bases for the integrals  $J_{\kappa\lambda}$  and  $K_{\kappa\lambda}$ ;  $\Psi_{\kappa}$  is again a four-component orbital spinor of one electron;  $\epsilon_{\kappa}$  is an eigenvalue of the operator  $F$  (and it is of course a scalar).

#### THE EXPANSION METHOD RELATIVISTIC SCF EQUATIONS FOR A CLOSED-SHELL GROUND STATE

Let us employ the expansion

$$\Psi_{\kappa} = \sum_{p=1}^m X_p C_{p\kappa}; \quad \kappa = 1, 2, \dots, N; \quad (18)$$

where

$$X_p \equiv \begin{pmatrix} \chi_{p1} \\ \chi_{p2} \\ \chi_{p3} \\ \chi_{p4} \end{pmatrix} \quad (19)$$

is a four-component basis spinor satisfying

$$\int X_p^* X_p dv = 1, \quad (20)$$

where

$$X_p^* \equiv (\bar{\chi}_{p1} \bar{\chi}_{p2} \bar{\chi}_{p3} \bar{\chi}_{p4}); \quad (21)$$

$m$  is the total number of basis spinors,  $m \geq N$ ;  $C_{p\kappa}$ 's are the coefficients of expansion. By applying the variational procedure we can easily derive the SCF equations of

the expansion method in the form

$$\mathbf{F} \mathbf{c}_{\kappa} = \epsilon_{\kappa} \mathbf{S} \mathbf{c}_{\kappa}; \quad (22)$$

where  $\mathbf{F}$  and  $\mathbf{S}$  are matrices, their elements being given as follows:

$$F_{pq} = \int X_p^* F X_q dv, \quad S_{pq} = \int X_p^* X_q dv; \quad (23)$$

the vector  $\mathbf{c}_{\kappa}$  is given by

$$\mathbf{c}_{\kappa} = \begin{pmatrix} C_{1\kappa} \\ C_{2\kappa} \\ \vdots \\ C_{m\kappa} \end{pmatrix}; \quad (24)$$

(the pseudo-eigenvalue  $\epsilon_{\kappa}$  is of course a scalar). Equations (22) form the basis for the SCF procedure applied to the expansion vectors  $\mathbf{c}_{\kappa}$ .

#### THE EXPRESSION FOR THE ENERGY $E_{00}$

We define the supermatrices  $\mathfrak{S}$  and  $\mathfrak{R}$  by giving their elements:

$$\mathfrak{S}_{pq,rs} = e^2 \int X_p^{\mu*} X_r^{\nu*} \frac{1}{r^{\mu\nu}} X_q^{\mu} X_s^{\nu} dv^{\mu\nu}, \quad (25)$$

$$\mathfrak{K}_{pq,rs} = e^2 \int X_p^{\mu*} X_r^{\nu*} \frac{1}{r^{\mu\nu}} X_s^{\mu} X_q^{\nu} dv^{\mu\nu}; \quad (26)$$

$\mathfrak{S}$  and  $\mathfrak{R}$  are symmetrical to the exchange  $pq \leftrightarrow rs$  and Hermitian to the simultaneous exchange  $p \leftrightarrow q$ ,  $r \leftrightarrow s$ . We construct the supermatrix  $\mathfrak{B}$  by

$$\mathfrak{B} = \mathfrak{S} - \mathfrak{R}. \quad (27)$$

From a set of vectors  $\mathbf{c}_{\kappa}$  satisfying, of course,

$$\mathbf{c}_{\kappa}^* \mathbf{S} \mathbf{c}_{\lambda} = \delta_{\kappa\lambda}, \quad (28)$$

we construct the density matrix

$$\mathbf{D} = \sum_{\kappa=1}^N \mathbf{c}_{\kappa} \mathbf{c}_{\kappa}^*. \quad (29)$$

With these definitions it is easy to show that

$$\mathbf{F} = \mathbf{H} + \mathfrak{B} \mathbf{D}, \quad (30)$$

where  $\mathbf{F}$ ,  $\mathbf{H}$ , and  $\mathbf{D}$  are to be understood as rearranged ( $\mathbf{F}$  and  $\mathbf{H}$  by rows,  $\mathbf{D}$  by columns) into the form of supervectors. ( $\mathbf{H}$  is given by  $H_{pq} = \int X_p^* H X_q dv$ .) Then, considering supervectors (all by rows),

$$E_{00} = \frac{1}{2} \sum_{\kappa=1}^N (H_{\kappa} + \epsilon_{\kappa}) = \frac{1}{2} (\mathbf{H} + \mathbf{F})^{\dagger} \mathbf{D}. \quad (31)$$

#### DEFINITIONS OF SOME INTEGRALS BASED ON SPINOR COMPONENTS

Denoting by  $\chi_{p\rho}$  the  $\rho$ th component ( $\rho = 1, 2, 3, 4$ ) of the  $p$ th basis spinor ( $p = 1, 2, \dots, m$ ) for the  $\mu$ th

electron we introduce the following notations:

$$\begin{aligned} \mathcal{S}_{pq,\rho\sigma} &= \int \bar{\chi}_{p\rho} \chi_{q\sigma} d^3v, \\ \mathcal{U}_{pq,\rho\sigma} &= \int \bar{\chi}_{p\rho} \varphi(\mathbf{r}^\mu) \chi_{q\sigma} d^3v, \\ \mathcal{P}_{x,pq,\rho\sigma} &= \int \bar{\chi}_{p\rho} p_x \chi_{q\sigma} d^3v, \end{aligned} \quad (32)$$

similarly for  $y$  and  $z$ ,

$$\mathcal{A}_{x,pq,\rho\sigma} = \int \bar{\chi}_{p\rho} A_x(\mathbf{r}^\mu) \chi_{q\sigma} d^3v, \quad (33)$$

similarly for  $y$  and  $z$ ;

$$\mathcal{B}_{pqrs,\rho\sigma\tau\varphi} = \int \frac{1}{r^{\mu\nu}} \bar{\chi}_{p\rho} \chi_{q\sigma} \bar{\chi}_{r\tau} \chi_{s\varphi} d^3v, \quad (34)$$

$$\mathcal{B}_{xy,pqrs,\rho\sigma\tau\varphi} = \int \frac{x^{\mu\nu} y^{\mu\nu}}{(r^{\mu\nu})^3} \bar{\chi}_{p\rho} \chi_{q\sigma} \bar{\chi}_{r\tau} \chi_{s\varphi} d^3v, \quad (35)$$

similarly for any other pair selected from  $x, y, z$ , provided that  $x^{\mu\nu}$  means the  $x$  component of  $\mathbf{r}^{\mu\nu}$ , etc.;

$$\mathcal{B}_{+-,pqrs,\rho\sigma\tau\varphi} = \int (\Omega_+^\mu \Omega_-^{\mu\nu}) \bar{\chi}_{p\rho} \chi_{q\sigma} \bar{\chi}_{r\tau} \chi_{s\varphi} d^3v, \quad (36)$$

similarly for any other pair selected from the three operators

$$\Omega_+^\mu, \quad \Omega_-^\mu, \quad \text{and} \quad \Omega_0,$$

where

$$\Omega_\pm^\mu = \frac{\partial}{\partial x^\mu} \pm i \frac{\partial}{\partial y^\mu}, \quad \Omega_0^\mu = \frac{\partial}{\partial z^\mu}.$$

#### ZEROth APPROXIMATION IN TERMS OF SPINOR COMPONENT INTEGRALS

The zeroth approximation is outlined by Eqs. (18), (22), (29), (30), and (31). [The difference between  $E_0$  and  $E_{00}$  is caused mainly by the correlation energy which is comparatively smaller than the relativistic effect for medium and heavier elements.<sup>12</sup> We are neglecting the Lorentz noninvariance of Eq. (2).]

The integrals occurring in this approximation can be expressed in terms of spinor component integrals.

$$S_{pq} = \sum_\rho^1 \mathcal{S}_{p\rho, q\rho}; \quad (37)$$

$$\begin{aligned} H_{pq} &= -e \sum_\rho^1 \mathcal{U}_{p\rho, q\rho} + mc^2 \sum_\rho^\beta \mathcal{S}_{p\rho, q\rho} \\ &+ (\sum_{\rho\sigma}^+ + \sum_{\rho\sigma}^-) [c(\mathcal{P}_{x,pq,\rho\sigma}) + e(\mathcal{A}_{x,pq,\rho\sigma})] \\ &+ i(\sum_{\rho\sigma}^+ - \sum_{\rho\sigma}^-) [c(\mathcal{P}_{y,pq,\rho\sigma}) + e(\mathcal{A}_{y,pq,\rho\sigma})] \\ &+ \sum_{\rho\sigma}^0 [c(\mathcal{P}_{z,pq,\rho\sigma}) + e(\mathcal{A}_{z,pq,\rho\sigma})]. \end{aligned} \quad (38)$$

To define in Eqs. (36) and (37) the summation operators over spinor components let us consider some spinor quantity, say,  $\mathcal{D}_{\rho\sigma}$ . Then we define

$$\begin{aligned} \sum_\rho^1 \mathcal{D}_{\rho\rho} &\equiv \sum_{\rho=1}^4 \mathcal{D}_{\rho\rho}; \\ \sum_\rho^\beta \mathcal{D}_{\rho\rho} &\equiv \mathcal{D}_{11} + \mathcal{D}_{22} - \mathcal{D}_{33} - \mathcal{D}_{44}; \\ (\sum^+ \pm \sum^-) \mathcal{D} &\equiv \sum^+ \mathcal{D} \pm \sum^- \mathcal{D}; \\ \sum_{\rho\sigma}^+ \mathcal{D}_{\rho\sigma} &\equiv \mathcal{D}_{23} + \mathcal{D}_{41}; \quad \sum_{\rho\sigma}^- \mathcal{D}_{\rho\sigma} \equiv \mathcal{D}_{14} + \mathcal{D}_{32}; \\ \sum_{\rho\sigma}^0 \mathcal{D}_{\rho\sigma} &\equiv \mathcal{D}_{13} - \mathcal{D}_{24} + \mathcal{D}_{31} - \mathcal{D}_{42}. \end{aligned} \quad (39)$$

[In electronic structure computations the rest energy  $mc^2$  of an electron in Eq. (37) could be appropriately subtracted.] In addition to the Eqs. (36) and (37), we have

$$\mathcal{I}_{pq,rs} = e^2 \sum_\rho^1 \sum_\sigma^1 \mathcal{B}_{pqrs,\rho\rho\sigma\sigma}; \quad (40)$$

$$\mathcal{K}_{pq,rs} = e^2 \sum_\rho^1 \sum_\sigma^1 \mathcal{B}_{psrq,\rho\rho\sigma\sigma}. \quad (41)$$

#### FIRST-ORDER APPROXIMATION IN TERMS OF SPINOR COMPONENT INTEGRALS

According to the first-order<sup>11</sup> perturbation theory, the total energy  $E$  is given by

$$E = E_0 + \Delta E, \quad (42)$$

where

$$\Delta E = \int \Phi^* B \Phi d^3v, \quad (43)$$

$$B = \frac{1}{2} \sum_{\substack{\mu,\nu=1 \\ \mu \neq \nu}}^N B^{\mu\nu}, \quad (44)$$

$$B^{\mu\nu} = -\frac{e^2}{2r^{\mu\nu}} \left[ \boldsymbol{\alpha}^\mu \cdot \boldsymbol{\alpha}^\nu + \frac{(\boldsymbol{\alpha}^\mu \cdot \mathbf{r}^{\mu\nu})(\boldsymbol{\alpha}^\nu \cdot \mathbf{r}^{\mu\nu})}{(r^{\mu\nu})^2} \right]. \quad (45)$$

It is easy to see that

$$\Delta E = \frac{1}{2} \sum_{\kappa,\lambda=1}^N (B_{1,\kappa\lambda} - B_{2,\kappa\lambda}), \quad (46)$$

where

$$B_{1,\kappa\lambda} = \int \Psi_\kappa^* \Psi_\lambda^* B^{\mu\nu} \Psi_\kappa \Psi_\lambda d^3v, \quad (47)$$

$$B_{2,\kappa\lambda} = \int \Psi_\kappa^* \Psi_\lambda^* B^{\mu\nu} \Psi_\lambda \Psi_\kappa d^3v. \quad (48)$$

After deriving explicit formulas for  $B_{1,\kappa\lambda}$  and  $B_{2,\kappa\lambda}$  and after some rearrangement of intermediate expressions in terms of integrals (34) into integrals (35), we finally

<sup>12</sup> A. Fröman, Rev. Mod. Phys. 32, 317 (1960).

obtain the expression

$$\begin{aligned} \Delta E = & -\frac{e^2}{4} \sum_{\kappa, \lambda=1}^N \sum_{p, q, r, s=1}^m \bar{C}_{p\kappa} \bar{C}_{r\lambda} (C_{s\kappa} C_{q\lambda} - C_{q\kappa} C_{s\lambda}) \\ & \times [2(4 \sum_{\rho\sigma, \tau\varphi}^{-+} + \sum_{\rho\sigma, \tau\varphi}^{00}) \mathfrak{B}_{pqrs, \rho\sigma\tau\varphi} \\ & - \sum_{\rho\sigma, \tau\varphi}^{++} \mathfrak{B}_{+,+, pqrs, \rho\sigma\tau\varphi} - \sum_{\rho\sigma, \tau\varphi}^{--} \mathfrak{B}_{-,-, pqrs, \rho\sigma\tau\varphi} \\ & - \sum_{\rho\sigma, \tau\varphi}^{00} \mathfrak{B}_{00, pqrs, \rho\sigma\tau\varphi} - 2(\sum_{\rho\sigma, \tau\varphi}^{-+} \mathfrak{B}_{+,-, pqrs, \rho\sigma\tau\varphi} \\ & + \sum_{\rho\sigma, \tau\varphi}^{+0} \mathfrak{B}_{+,0, pqrs, \rho\sigma\tau\varphi} + \sum_{\rho\sigma, \tau\varphi}^{-0} \mathfrak{B}_{-,0, pqrs, \rho\sigma\tau\varphi})]; \quad (48) \end{aligned}$$

the sums (summation operators) are to be understood in the sense of the following example:

$$\sum_{\rho\sigma, \tau\varphi}^{-+} = \sum_{\rho\sigma}^{-} \sum_{\tau\varphi}^{+}. \quad (49)$$

#### BASIS SPINORS AND THE NUCLEAR POTENTIAL

The question arises what kind of basis spinors (19) should be used for computations. If we used exact solutions of the Dirac equation then the evaluation of corresponding integrals over hypergeometric functions would be rather tedious, particularly if we consider voluminous expressions arising from linear combinations for many-electron systems. It seems to be plausible to use Slater-type orbitals for the components of basis spinors; then the absolute relativistic SCF solution can be approached by taking sufficiently large set of basis spinors.<sup>13</sup> Using Slater-type orbitals would enable the use of experiences obtained in computations of nonrelativistic integrals.

The unnormalized components of the basis spinors (19) will be denoted by  $u_1, u_2, u_3$ , and  $u_4$ ; we shall use for them the following expressions<sup>14</sup>:

$$\begin{aligned} j = l + \frac{1}{2}; \quad u_1 &= [(l+m+\frac{1}{2})/(2l+1)]^{1/2} g(r) Y_{l, m-1/2}(\vartheta, \varphi), \\ u_2 &= -[(l-m+\frac{1}{2})/(2l+1)]^{1/2} g(r) Y_{l, m+1/2}(\vartheta, \varphi), \\ u_3 &= -[(l-m+\frac{3}{2})/(2l+3)]^{1/2} i f(r) Y_{l+1, m-1/2}(\vartheta, \varphi), \\ u_4 &= -[(l+m+\frac{3}{2})/(2l+3)]^{1/2} i f(r) Y_{l+1, m+1/2}(\vartheta, \varphi); \end{aligned} \quad (50)$$

$$\begin{aligned} j = l - \frac{1}{2}; \quad u_1 &= [(l-m+\frac{1}{2})/(2l+1)]^{1/2} g(r) Y_{l, m-1/2}(\vartheta, \varphi), \\ u_2 &= [(l+m+\frac{1}{2})/(2l+1)]^{1/2} g(r) Y_{l, m+1/2}(\vartheta, \varphi), \\ u_3 &= -[(l+m-\frac{1}{2})/(2l-1)]^{1/2} i f(r) Y_{l-1, m-1/2}(\vartheta, \varphi), \\ u_4 &= [(l-m-\frac{1}{2})/(2l-1)]^{1/2} i f(r) Y_{l-1, m+1/2}(\vartheta, \varphi). \end{aligned} \quad (51)$$

$$\begin{aligned} 1S_{1/2}: \quad g &= e^{-\xi_1 r}, \\ f &= -[(1-\varepsilon_1)/(1+\varepsilon_1)]^{1/2} g, \quad \varepsilon_1 = [1+(\alpha Z/\gamma_1)^2]^{-1/2}, \quad \gamma_1 = (1-\alpha^2 Z^2)^{1/2}. \end{aligned} \quad (52.1)$$

$$\begin{aligned} 2S_{1/2}: \quad g &= r e^{-\xi_2 r}, \\ f &= -[(1-\varepsilon_2)/(1+\varepsilon_2)]^{1/2} [(N_2+2)/N_2] g, \quad \varepsilon_2 = \{1+[\alpha Z/(1+\gamma_1)]^2\}^{-1/2}, \quad N_2 = [2(1+\gamma_1)]^{1/2}. \end{aligned} \quad (52.2)$$

$$\begin{aligned} 2P_{1/2}: \quad g &= r e^{-\xi_2 r}, \\ f &= -[(1-\varepsilon_2)/(1+\varepsilon_2)]^{1/2} [N_2/(N_2-2)] g. \end{aligned} \quad (52.3)$$

$$\begin{aligned} 2P_{3/2}: \quad g &= r e^{-\xi_3 r}, \\ f &= -[(1-\varepsilon_3)/(1+\varepsilon_3)]^{1/2} g, \quad \varepsilon_3 = [1+(\alpha Z/\gamma_2)^2]^{-1/2}, \quad \gamma_2 = (4-\alpha^2 Z^2)^{1/2}. \end{aligned} \quad (52.4)$$

In these expression  $j, m$ , and  $l$  are the quantum numbers of the total angular momentum, of the  $z$  component of the total angular momentum and of the orbital angular momentum, respectively.  $Y_{l,m}(\vartheta, \varphi)$  is a usual spherical harmonic of the polar angles  $\vartheta$  and  $\varphi$ .  $r$  is the distance of an electron from the nucleus.  $\xi_{nj}$  is an effective exponent depending on the principal quantum number  $n$  and on  $j$ .  $Z$  is a nuclear charge.  $\alpha$  is the fine structure constant.

In Eqs. (52), each function  $f(r)$  is approximated by its function  $g(r)$  multiplied by a proportionality constant obtained from an exact Dirac solution by a reduction to the zero distance from the nucleus. This approximation is justified by the fact that the greatest differences<sup>13</sup>

between the relativistic and nonrelativistic orbitals occur for very small distances from the nucleus, and by a computational convenience. Equations (52) are actually suggesting only initial trial quantities for an SCF procedure. In an actual computation further improvement would be obtained by a variational optimization of the effective exponents  $\xi_{nj}$  as well as of the proportionality constants  $f/g$  (later introduced as  $C_{n_p j_p l_p Z \rho}$ ).

For a better description of the atomic situation it is

<sup>13</sup> The comparison of Schrödinger and Dirac orbitals is discussed in Ref. 1, Sec. 14 $\delta$ .

<sup>14</sup> Approximated on the base of the exact solution of the Dirac equation as given in Ref. 1, Sec. 14; for "higher" spinors see W. B. Payne, Ph.D. thesis, Louisiana State University, 1955 (unpublished).

recommendable to consider a finite size of the nucleus with its specific nuclear potential.<sup>15</sup> Then it is possible to justify the use of "nonfractional principal quantum numbers" used in our approximation in terms of Slater type orbitals.<sup>13</sup> The introduction of the specific nuclear magnetization and charge distribution has its importance in a more accurate calculation of the hyperfine structure.<sup>15</sup>

Considering the calculational convenience, the form of final formulas and the Lorentz noninvariance of Eq. (2), it seems to be a matter of discussion if a basis spinor should be taken as a fixed combination of two spinors of the same  $j$  for  $j=l_1+\frac{1}{2}$  and  $j=l_2-\frac{1}{2}$ , or if this should be taken care of by an SCF expansion (as it is assumed in this work).

### CONCLUDING REMARKS

The specific case of an atomic system is treated in the appendices.

The treatment presented in this article is, of course, not to be considered closed or completed. It rather develops a background on the base of which further new developments can be imagined.

In particular, a detailed description of the symmetry restrictions,<sup>16</sup> of the open-shell theory and of other features, as well as an extension to molecular and solid state systems, are subjects for a future treatment.

### APPENDIX I

Now we shall consider an atomic system (without an external field). We shall present the formulas for the atomic integrals occurring in the final expressions both for the zeroth and for the first-order approximation.

Every basis spinor  $X_p$  will be considered as being determined by  $n_p, j_p, m_p, l_p, \zeta_p$  and  $Z$ , where the first five quantities are assigned to the  $p$ th basis spinor and represent the usual four quantum numbers and the effective exponent.

From the formulas (50) and (51) we can see that the  $\rho$ th component of a basis spinor  $X_p$  can be written as follows:

$$\begin{aligned} \chi_{p\rho} &= N_p^{-1/2} u_\rho[\rho] \\ &= N_p^{-1/2} C'(j_p m_p l_p; \rho) \mathcal{R}_{n_p j_p l_p \zeta_p Z \rho}(r) \\ &\quad \times \mathcal{Y}_{j_p m_p l_p \rho}(\vartheta, \varphi), \end{aligned} \quad (53)$$

where  $u_\rho[\rho]$  is the  $\rho$ th component of an unnormalized  $p$ th basis spinor of the form (50) or (51);  $N_p$  is the normalization factor (to be determined) for the  $p$ th basis spinor;  $\mathcal{R}$  is given either by  $g(r)$  or  $f(r)$ ;  $\mathcal{Y}$  is given by the appropriate spherical harmonic;  $C'$  is given by the remaining factors in the spinor component considered.

More explicitly, for  $\mathcal{R}$  we can write

$$\begin{aligned} \mathcal{R}_{n_p j_p l_p \zeta_p Z \rho}(r) &= \mathcal{C}_{n_p j_p l_p Z \rho} g_{n_p \zeta_p}(r) \\ &\equiv \mathcal{C}_{n_p j_p l_p Z \rho} r^{n_p-1} e^{-\zeta_p r}; \end{aligned} \quad (54)$$

where

$$\mathcal{C}_{n_p j_p l_p Z \rho} = 1 \quad \text{for } \rho = 1, 2$$

(independently of other indices);

$$\mathcal{C}_{n_p j_p l_p Z \rho} \neq 1 \quad \text{for } \rho = 3, 4$$

and its initial trial value is given on the base of formulas (52) or their analogs for "higher" spinors.<sup>14</sup>

The normalization factor  $N_p$  is determined by the requirement (20), or

$$N_p^{-1} \sum_\rho \int \bar{u}_\rho[\rho] u_\rho[\rho] dv = 1. \quad (55)$$

Using (53) and (54) we find that

$$N_p = \frac{(2n_p)!}{(2\zeta_p)^{2n_p+1}} \sum_\rho |C'(j_p m_p l_p; \rho)|^2 (\mathcal{C}_{n_p j_p l_p Z \rho})^2. \quad (56)$$

In order to obtain the formulas for the atomic integrals in a condensed form we introduce the notation

$$\chi_{p\rho} = N(Z, p\rho) r^{n_p-1} e^{-\zeta_p r} Y_{l_p, m_p \rho}(\vartheta, \varphi), \quad (57)$$

where

$$N(Z, p\rho) = N_p^{-1/2} C'(j_p m_p l_p; \rho) \mathcal{C}_{n_p j_p l_p Z \rho}; \quad (58)$$

$l_p$  and  $m_p$  are "orbital and magnetic quantum numbers," respectively, describing the spherical harmonic of the  $\rho$ th component of the  $p$ th basis spinor. We require that  $l_p \geq 0$ ,  $-l_p \leq m_p \leq l_p$ ; if this is not fulfilled the spherical harmonic  $Y_{l_p, m_p \rho}$  vanishes<sup>17</sup> and hence also an integral in whose integrand it occurs; our formulas for the integrals were derived assuming that the requirement mentioned is fulfilled.

For the one-electron integrals the following formulas were derived (employing the Kronecker's  $\delta_{ij}$  notation):

$$S_{pq, \rho\sigma} = \delta_{l_p, l_q} \delta_{m_p, m_q} \bar{N}(Z, p\rho) N(Z, q\sigma) \frac{(n_p + n_q)!}{(\zeta_p + \zeta_q)^{n_p + n_q + 1}}; \quad (59)$$

$$U_{pq, \rho\sigma} = \delta_{l_p, l_q} \delta_{m_p, m_q} Z e \bar{N}(Z, p\rho) N(Z, q\sigma) \frac{(n_p + n_q - 1)!}{(\zeta_p + \zeta_q)^{n_p + n_q}}, \quad (60)$$

<sup>15</sup> H. H. Stroke, R. J. Blin-Stoyle, and V. Jaccarino, Phys. Rev. **123**, 1326 (1961).

<sup>16</sup> Mentioned in Appendix III.

<sup>17</sup> A related discussion is in Ref. 1, Sec. 14a.

(for a point nucleus; a related expression would be obtained for a finite size nucleus);

$$\begin{aligned} \mathcal{P}_{z,pq,\rho\sigma} = & -i\hbar\delta_{m_{pp},m_{q\sigma}}\bar{N}(Z,p\rho)N(Z,q\sigma)\frac{(n_p+n_q-1)!}{(\zeta_p+\zeta_q)^{n_p+n_q}} \\ & \times \left[ \delta_{l_{pp},l_{q\sigma}+1} \left( n_q - l_{q\sigma} - 1 - \zeta_p \frac{n_p+n_q}{\zeta_p+\zeta_q} \right) \left( \frac{(l_{q\sigma}+m_{q\sigma}+1)(l_{q\sigma}-m_{q\sigma}+1)}{(2l_{q\sigma}+3)(2l_{q\sigma}+1)} \right)^{1/2} \right. \\ & \left. + \delta_{l_{pp},l_{q\sigma}-1} \left( n_q + l_{q\sigma} - \zeta_q \frac{n_p+n_q}{\zeta_p+\zeta_q} \right) \left( \frac{(l_{q\sigma}+m_{q\sigma})(l_{q\sigma}-m_{q\sigma})}{(2l_{q\sigma}+1)(2l_{q\sigma}-1)} \right)^{1/2} \right]; \quad (61) \end{aligned}$$

$$\begin{aligned} \mathcal{P}_{x,pq,\rho\sigma} \pm i\mathcal{P}_{y,pq,\rho\sigma} = & -i\hbar\delta_{m_{pp},m_{q\sigma}\pm 1}\bar{N}(Z,p\rho)N(Z,q\sigma)\frac{(n_p+n_q-1)!}{(\zeta_p+\zeta_q)^{n_p+n_q}} \\ & \times \left[ \pm \delta_{l_{pp},l_{q\sigma}\pm 1} \left( n_q - l_{q\sigma} - 1 - \zeta_q \frac{n_p+n_q}{\zeta_p+\zeta_q} \right) \left( \frac{(l_{q\sigma}\pm m_{q\sigma}+2)(l_{q\sigma}\pm m_{q\sigma}+1)}{(2l_{q\sigma}+3)(2l_{q\sigma}+1)} \right)^{1/2} \right. \\ & \left. \mp \delta_{l_{pp},l_{q\sigma}-1} \left( n_q + l_{q\sigma} - \zeta_q \frac{n_p+n_q}{\zeta_p+\zeta_q} \right) \left( \frac{(l_{q\sigma}\mp m_{q\sigma})(l_{q\sigma}\mp m_{q\sigma}-1)}{(2l_{q\sigma}+1)(2l_{q\sigma}-1)} \right)^{1/2} \right]. \quad (62) \end{aligned}$$

In order to present the formulas for the two-electron integrals, let us introduce some auxiliary quantities.<sup>18</sup>

$$\begin{aligned} \mathfrak{X}(Z; pqrs; \rho\sigma\tau\varphi) = & \frac{1}{2} [1 + (-1)^{l_{p\rho}+l_{q\sigma}+l_{r\tau}+l_{s\varphi}}] (-1)^{m_{r\tau}-m_{s\varphi}} \\ & \times \left[ \frac{(2l_{q\sigma}+1)(2l_{s\varphi}+1)}{(2l_{p\rho}+1)(2l_{r\tau}+1)} \right]^{1/2} \bar{N}(Z,p\rho)N(Z,q\sigma)\bar{N}(Z,r\tau)N(Z,s\varphi); \quad (63) \end{aligned}$$

$$V_i(x) = x^{-i-1}i!; \quad (i! \equiv 0, \text{ if } i < 0); \quad (64)$$

$$C_{\alpha\beta}(t) = (\alpha! \beta!)^{-1} t^{\alpha+1} \int_0^\infty du u^\alpha e^{-tu} \int_0^u dv v^\beta e^{-v}, \quad (65)$$

which can also be written as<sup>19</sup>

$$C_{\alpha\beta}(t) = (1+t)^{-\alpha-\beta-1} \sum_{\lambda=0}^{\alpha+\beta+1} \binom{\alpha+\beta+1}{\lambda} t^\lambda, \quad (66)$$

as can be seen by an induction;  $C(j_1, j_2, j; m_1, m_2)$  is a Clebsch-Gordan coefficient as defined by Rose<sup>20</sup>;

$$\begin{aligned} I_1(pqrs; \rho\sigma\tau\varphi | l) = & \{ (2l+3)^{-1} [4l(l+2)+3] V_{n_r+n_s-l-1}(\zeta_r+\zeta_s) V_{n_p+n_q+l}(\zeta_p+\zeta_q) C_{n_r+n_s-l-1, n_p+n_q+l}[(\zeta_r+\zeta_s)/(\zeta_p+\zeta_q)] \\ & - (2l+1) V_{n_r+n_s-l+1}(\zeta_r+\zeta_s) V_{n_p+n_q+l-2}(\zeta_p+\zeta_q) C_{n_r+n_s-l+1, n_p+n_q+l-2}[(\zeta_r+\zeta_s)/(\zeta_p+\zeta_q)] \} \\ & \times C(l-2, l_{q\sigma}, l_{p\rho}; m_{p\rho}-m_{q\sigma}, m_{q\sigma}) C(l-2, l_{q\sigma}, l_{p\rho}; 00) C(l, l_{s\varphi}, l_{r\tau}; m_{r\tau}-m_{s\varphi}, m_{s\varphi}) C(l, l_{s\varphi}, l_{r\tau}; 00); \quad (67) \end{aligned}$$

$$\begin{aligned} I_0(pqrs; \rho\sigma\tau\varphi | l) = & 2 \{ V_{n_p+n_q-l-1}(\zeta_p+\zeta_q) V_{n_r+n_s+l}(\zeta_r+\zeta_s) C_{n_p+n_q-l-1, n_r+n_s+l}[(\zeta_p+\zeta_q)/(\zeta_r+\zeta_s)] \\ & + V_{n_r+n_s-l-1}(\zeta_r+\zeta_s) V_{n_p+n_q+l}(\zeta_p+\zeta_q) C_{n_r+n_s-l-1, n_p+n_q+l}[(\zeta_r+\zeta_s)/(\zeta_p+\zeta_q)] \} \\ & \times C(l, l_{q\sigma}, l_{p\rho}; m_{p\rho}-m_{q\sigma}, m_{q\sigma}) C(l, l_{q\sigma}, l_{p\rho}; 00) C(l, l_{s\varphi}, l_{r\tau}; m_{r\tau}-m_{s\varphi}, m_{s\varphi}) C(l, l_{s\varphi}, l_{r\tau}; 00); \quad (68) \end{aligned}$$

$$\begin{aligned} I_{-1}(pqrs; \rho\sigma\tau\varphi | l) = & \{ -(2l+1) V_{n_p+n_q-l-1}(\zeta_p+\zeta_q) V_{n_r+n_s+l}(\zeta_r+\zeta_s) C_{n_p+n_q-l-1, n_r+n_s+l}[(\zeta_p+\zeta_q)/(\zeta_r+\zeta_s)] \\ & + (2l+3)^{-1} [4l(l+2)+3] V_{n_p+n_q-l-3}(\zeta_p+\zeta_q) V_{n_r+n_s+l+2}(\zeta_r+\zeta_s) C_{n_p+n_q-l-3, n_r+n_s+l+2}[(\zeta_p+\zeta_q)/(\zeta_r+\zeta_s)] \} \\ & \times C(l+2, l_{q\sigma}, l_{p\rho}; m_{p\rho}-m_{q\sigma}, m_{q\sigma}) C(l+2, l_{q\sigma}, l_{p\rho}; 00) C(l, l_{s\varphi}, l_{r\tau}; m_{r\tau}-m_{s\varphi}, m_{s\varphi}) C(l, l_{s\varphi}, l_{r\tau}; 00). \quad (69) \end{aligned}$$

<sup>18</sup> The functions  $V_i(x)$  and  $C_{\alpha\beta}(t)$  were also used for the nonrelativistic treatment. See, e.g., C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960).

<sup>19</sup> C. C. J. Roothaan (private communication).

<sup>20</sup> M. E. Rose, *Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

For the two-electron integrals the following formulas were derived<sup>21</sup>:

$$\mathfrak{B}_{pqrs, \rho\sigma\tau\varphi} = \frac{1}{2} \delta_{m_{pp}, m_{rr}, m_{q\sigma} + m_{s\varphi}} \mathfrak{U}(Z; pqrs; \rho\sigma\tau\varphi) \sum_{l=\max(|l_{pp}-l_{q\sigma}|, |l_{rr}-l_{s\varphi}|)}^{l=\min(l_{pp}+l_{q\sigma}, l_{rr}+l_{s\varphi})} I_0(pqrs; \rho\sigma\tau\varphi | l); \quad (70)$$

$$\mathfrak{B}_{\alpha\beta, pqrs, \rho\sigma\tau\varphi} = \delta_{m_{pp}+m_{rr}, m_{q\sigma}+m_{s\varphi}+m_{\alpha\beta}} \mathfrak{U}(Z; pqrs; \rho\sigma\tau\varphi) \times \sum_{k=-1, 0, 1} \sum_{l=\max(|l_{pp}-l_{q\sigma}|+2k, |l_{rr}-l_{s\varphi}|)}^{l=\min(l_{pp}+l_{q\sigma}+2k, l_{rr}+l_{s\varphi})} a_k(\alpha\beta; rs; \tau\varphi | l) I_k(pqrs; \rho\sigma\tau\varphi | l), \quad (71)$$

where  $\alpha\beta$  can become any of the combinations  $++$ ,  $--$ ,  $00$ ,  $+-$ ,  $+0$ ,  $-0$ , and the summation over  $l$  in (71) is defined to be equal to zero if the upper limit becomes smaller than the lower limit. The explicit expressions for the coefficients  $a_k(\alpha\beta; rs; \tau\varphi | l)$  which will now be written (for brevity) as  $a_k(\alpha\beta)$ , and the expressions for  $m_{\alpha\beta}$ , are as follows:

$$\begin{aligned} m_{++} = 2; \quad a_{-1}(++) &= [(2l+1)(2l+3)]^{-1} \left[ \prod_{i=1, 2, 3, 4} (l - m_{rr} + m_{s\varphi} + i) \right]^{1/2}; \\ a_0(++) &= -(2l+1)^{-1} [(2l-1)^{-1} + (2l+3)^{-1}] \left[ \prod_{i=0, 1} (l + m_{rr} - m_{s\varphi} - i)(l - m_{rr} + m_{s\varphi} + 1 + i) \right]^{1/2}; \\ a_1(++) &= [(2l+1)(2l-1)]^{-1} \left[ \prod_{i=0, 1, 2, 3} (l + m_{rr} - m_{s\varphi} - i) \right]^{1/2}; \end{aligned} \quad (72.1)$$

$$\begin{aligned} m_{--} = -2; \quad a_{-1}(--) &= [(2l+1)(2l+3)]^{-1} \left[ \prod_{i=1, 2, 3, 4} (l + m_{rr} - m_{s\varphi} + i) \right]^{1/2}; \\ a_0(--) &= -(2l+1)^{-1} [(2l-1)^{-1} + (2l+3)^{-1}] \left[ \prod_{i=0, 1} (l - m_{rr} + m_{s\varphi} - i)(l + m_{rr} - m_{s\varphi} + 1 + i) \right]^{1/2}; \\ a_1(--) &= [(2l+1)(2l-1)]^{-1} \left[ \prod_{i=0, 1, 2, 3} (l - m_{rr} + m_{s\varphi} - i) \right]^{1/2}; \end{aligned} \quad (72.2)$$

$$\begin{aligned} m_{00} = 0; \quad a_{-1}(00) &= [(2l+1)(2l+3)]^{-1} \left[ \prod_{i=1, 2} (l + m_{rr} - m_{s\varphi} + i)(l - m_{rr} + m_{s\varphi} + i) \right]^{1/2}; \\ a_0(00) &= (2l+1)^{-1} [(2l-1)^{-1} (l + m_{rr} - m_{s\varphi})(l - m_{rr} + m_{s\varphi}) \\ &\quad + (2l+3)^{-1} (l + m_{rr} - m_{s\varphi} + 1)(l - m_{rr} + m_{s\varphi} + 1)]; \\ a_1(00) &= [(2l+1)(2l-1)]^{-1} \left[ \prod_{i=0, 1} (l - m_{rr} + m_{s\varphi} - i)(l + m_{rr} - m_{s\varphi} - i) \right]^{1/2}; \end{aligned} \quad (72.3)$$

$$\begin{aligned} m_{+-} = 0; \quad a_{-1}(+-) &= -[(2l+1)(2l+3)]^{-1} \left[ \prod_{i=1, 2} (l + m_{rr} - m_{s\varphi} + i)(l - m_{rr} + m_{s\varphi} + i) \right]^{1/2} = -a_{-1}(00); \\ a_0(+-) &= (2l+1)^{-1} [(2l-1)^{-1} \prod_{i=0, 1} (l - m_{rr} + m_{s\varphi} - i) + (2l+3)^{-1} \prod_{i=1, 2} (l + m_{rr} - m_{s\varphi} + i)]; \\ a_1(+-) &= -[(2l+1)(2l-1)]^{-1} \left[ \prod_{i=0, 1} (l - m_{rr} + m_{s\varphi} - i)(l + m_{rr} - m_{s\varphi} - i) \right]^{1/2} = -a_1(00); \end{aligned} \quad (72.4)$$

$$\begin{aligned} m_{+0} = 1; \quad a_{-1}(+0) &= [(2l+1)(2l+3)]^{-1} (l + m_{rr} - m_{s\varphi} + 1)^{1/2} \left[ \prod_{i=1, 2, 3} (l - m_{rr} + m_{s\varphi} + i) \right]^{1/2}; \\ a_0(+0) &= (2l+1)^{-1} (l + m_{rr} - m_{s\varphi})^{1/2} (l - m_{rr} + m_{s\varphi} + 1)^{1/2} \\ &\quad \times [(2l-1)^{-1} (l - m_{rr} + m_{s\varphi}) - (2l+3)^{-1} (l + m_{rr} - m_{s\varphi} + 1)]; \\ a_1(+0) &= -[(2l+1)(2l-1)]^{-1} (l - m_{rr} + m_{s\varphi})^{1/2} \left[ \prod_{i=0, 1, 2} (l + m_{rr} - m_{s\varphi} - i) \right]^{1/2}; \end{aligned} \quad (72.5)$$

$$\begin{aligned} m_{-0} = -1; \quad a_{-1}(-0) &= -[(2l+1)(2l+3)]^{-1} (l - m_{rr} + m_{s\varphi} + 1)^{1/2} \left[ \prod_{i=1, 2, 3} (l + m_{rr} - m_{s\varphi} + i) \right]^{1/2}; \\ a_0(-0) &= (2l+1)^{-1} (l - m_{rr} + m_{s\varphi})^{1/2} (l + m_{rr} - m_{s\varphi} + 1)^{1/2} \\ &\quad \times [(2l+3)^{-1} (l - m_{rr} + m_{s\varphi} + 1) - (2l-1)^{-1} (l + m_{rr} - m_{s\varphi})]; \\ a_1(-0) &= [(2l+1)(2l-1)]^{-1} (l + m_{rr} - m_{s\varphi})^{1/2} \left[ \prod_{i=0, 1, 2} (l - m_{rr} + m_{s\varphi} - i) \right]^{1/2}. \end{aligned} \quad (72.6)$$

<sup>21</sup> A description of the derivation is given in Appendix II.



## APPENDIX II

In order to outline the derivation of the formulas for the two-electron atomic integrals let us start with  $\mathcal{B}_{pqrs,\rho\sigma\tau\varphi}$ . This integral is calculated by using the expansion<sup>22</sup> of  $1/r^{\mu\nu}$  in terms of spherical harmonics and hence splitting the integral into products of feasible radial parts and angular parts. A radial part is then calculated in a customary way.<sup>23</sup> An angular part can be considered as a product of two integrals, each integral taken over the product of three spherical harmonics; for such integrals a formula given by Rose<sup>24</sup> can be used. Then we realize that<sup>25</sup>

$$C(l_1, l_2, l; m_1, m_2, m) = 0, \quad (73)$$

unless

$$\Delta(l_1 l_2 l) \quad (74)$$

is valid, and unless

$$m = m_1 + m_2. \quad (75)$$

Furthermore,

$$C(l_1, l_2, l; 000) = 0 \quad (76)$$

unless  $l_1 + l_2 + l$  is even. Hence the total expression for the integral  $\mathcal{B}_{pqrs,\rho\sigma\tau\varphi}$  must consist of:

(1) A summation over  $l$  only between the limits satisfying  $\Delta(l_1 l_2 l)$  for each  $C(l_1, l_2, l; m_1, m_2, m)$ .

(2) Two Kronecker's symbols of the type  $\delta_{m, m_1 + m_2}$  which can be contracted into one symbol.

(3) The expression of the type

$$\frac{1}{2}[1 + (-1)^{l_1 + l_2 + l_3 + l_4}], \quad (77)$$

for each product  $C(l_1, l_2, l; 00) C(l_3, l_4, l; 00)$ . Since (76) and (77) require that  $l_1 + l_2$  and  $l_3 + l_4$  be simultaneously either even or odd it is necessary to perform the summation over  $l$  in the steps of two. The formula (70) is finally obtained with the help of the definitions (63) and (68).

Now we consider the integral  $\mathcal{B}_{\alpha\beta, pqrs, \rho\sigma\tau\varphi}$ . This integral is of a similar type as  $\mathcal{B}_{pqrs, \rho\sigma\tau\varphi}$ , except that  $1/r^{\mu\nu}$  is substituted by  $\Omega_\alpha^\mu \Omega_\beta^\nu r^{\mu\nu}$ . We are looking for an expansion of  $r^{\mu\nu}$  in terms of spherical harmonics in order to facilitate the application of the operators  $\Omega_\pm^\mu$  and  $\Omega_0^\mu$ . This expansion can easily be obtained<sup>26</sup> through multiplying the expansion<sup>27</sup> for  $1/r^{\mu\nu}$  in terms of

Legendre polynomials by

$$(r^{\mu\nu})^2 = (r^\mu)^2 + (r^\nu)^2 - 2r^\mu r^\nu \cos\vartheta^{\mu\nu}; \quad (78)$$

then we can come to the expansion

$$r^{\mu\nu} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} b_l(r^\mu, r^\nu) Y_{lm}(\vartheta^\mu, \varphi^\mu) \bar{Y}_{lm}(\vartheta^\nu, \varphi^\nu), \quad (79)$$

where

$$b_l(r^\mu, r^\nu) = \frac{(r^<)^l}{(r^>)^{l+1}} \left[ (r^\mu)^2 + (r^\nu)^2 - 2r^\mu r^\nu \left( \frac{l}{2l-1} \frac{r^>}{r^<} + \frac{l+1}{2l+3} \frac{r^<}{r^>} \right) \right]. \quad (80)$$

Now the application of the operators  $\Omega_\pm^\mu$  and  $\Omega_0^\mu$  on the expansion (79) for  $r^{\mu\nu}$  can easily be performed, using the known formulas.<sup>28</sup> Hence every integral  $\mathcal{B}_{\alpha\beta, pqrs, \rho\sigma\tau\varphi}$  is split into the four addends, each addend representing an integral of a type similar to  $\mathcal{B}_{pqrs, \rho\sigma\tau\varphi}$ , however, with a more complicated radial part caused by the addends in (80). Using a similar technique as for the derivation of the formula (70), one obtains, after a straightforward calculation, formulas (71) and (72).

## APPENDIX III

Regarding the solving of Eqs. (22) it is to be remarked that the group theory could be utilized in a similar way as in the nonrelativistic case. This can be associated with a requirement that, e.g., in an atomic system without an external field, the properly optimized spinors transform under the  $(2j+1)$ -dimensional representations  $D^{(j)}(\{\alpha\beta\gamma\})$ ,  $j$  half-integer, of the rotation group.<sup>29,30</sup> Also, the "averaging out" over the subspecies represented by the quantum number  $m$ , might be utilized similarly as in the nonrelativistic SCF calculation.<sup>3</sup>

## ACKNOWLEDGMENT

The author expresses his indebtedness to the staff of the Department of Physics, DePaul University, Chicago, Illinois.

<sup>28</sup> Reference 1, formulas (A37)–(A39).

<sup>29</sup> B. L. van der Waerden, *Die gruppentheoretische Methode in der Quantenmechanik* (Lithoprinted by Edwards Brothers, Inc., Ann Arbor, Michigan, 1944), p. 100; E. O. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), Chap. 15; M. Hamermesh, *Group Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1962), Sec. 11–5.

<sup>30</sup> Furthermore, as we know, the form of Eq. (22) is similar to the one for the nonrelativistic SCF expansion method (for closed shells), which might enable a utilization of some computer routines used in current programs.

<sup>22</sup> H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 371.

<sup>23</sup> See Ref. 22, p. 103 and definitions (64) and (65) of this article.

<sup>24</sup> Reference 20, formula (4.34).

<sup>25</sup> For the definition of  $\Delta(l_1 l_2 l_3)$  see Ref. 20, p. 36; for an explanation of (74), (75), and (76) see Ref. 20, pp. 34, 36, and 42.

<sup>26</sup> C. C. J. Roothaan (private communication).

<sup>27</sup> Reference 22, Appendix V.