Theoret. Chim. Acta (Berl.) 54, 35–51 (1979)

THEORETICA CHIMICA ACTA

Approximate Relativistic Hartree–Fock Equations and Their Solution within a Minimum Basis Set of Slater-Type Functions*

Franz Rosicky

Institut für theoretische Chemie und Strahlenchemie, Universität Wien, Währingerstr. 17, A-1090 Wien, Austria

Franz Mark

Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, Stiftstr. 34–36, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

Relativistic closed-shell atoms are treated by the use of a specific approximation for the small component of the one-electron Dirac spinors. It is assumed that the large and the small component are interconnected by a parameter-dependent relation which is formally analogous to that of the one-electron system. Subject to this constraint, the total energy is varied with respect to the large components. The resulting eigenvalue equations for the large components contain only regular potential terms and reduce to the familiar Hartree–Fock equations in the limit of infinite velocity of light. Analytical solution of these approximate relativistic Hartree–Fock equations is achieved using a minimum basis set of Slater-type functions for the expansion of the radial part of the large components. Total relativistic energies, orbital energies, orbital exponents and mean radii are calculated for the ground states of He, Be, Ne, Mg, Ar, Kr, Xe and Cu^+.

Key words: Relativistic Hartree–Fock – Closed-shell atoms

1. Introduction

Numerical solutions of the relativistic Hartree–Fock (RHF) equations (for a review see [1]) have been obtained for many atomic systems [2–7], and compilations of relevant data exist [8–10]. However, analytical solutions of the RHF equations within the LCAO approximation [11–13] were obtained only for a few atoms [11, 13]. The predominant use of the numerical integration method is mainly due to the fact that in the LCAO-RHF method large basis sets are needed since the number of one-electron states is almost doubled, and furthermore the large as well as the small

---

* Dedicated to Prof. O. E. Polansky on occasion of his 60th birthday.

0040-5744/79/0054/0035/$03.40

components of the Dirac orbitals have to be represented adequately. Thus, Kim [11] remarks "that the so-called minimum basis set relativistic wave functions lead to results so bad that it makes no sense to do any relativistic calculations with them".

In the following, an attempt is made to reduce the difficulties arising from the increased size of the basis set by taking the approximation of an *a priori* relationship between the large and the small component of the one-electron Dirac orbitals. This functional relation is, in the case of a many-electron atom, chosen in analogy to that one which for the one-electron problem is obtained by the elimination method [14]. Given this functional relation an implicit eigenvalue problem for the large component is derived by varying the total energy with respect to all large components only. According to this approximation only regular potential terms in the RHF equations appear which in the limit of infinite velocity of light reduce directly to the nonrelativistic Hartree–Fock (NRHF) equations.

In order to estimate the numerical accuracy of the proposed approximation, calculations for some relativistically closed-shell atoms are performed using a minimum basis set (MBS) of Slater-type functions (STFs) for the radial part of the large components. The numerical results for relativistic total energy corrections and orbital energies are in fairly good agreement with those of numerical RHF calculations.

2. Approximate Relativistic Hartree–Fock Equations

2.1. The Functional Relation between the Large and the Small Components

For an atom with N electrons and a nuclear charge Z the Hamiltonian (in a.u.) is taken to be

$$H = \sum_{i}^{N} h_i + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{1}$$

where h_i represents the Dirac-Hamiltonian for the ith electron

$$h_i = c^2\beta_i' + c\boldsymbol{\alpha}_i\boldsymbol{p}_i - \frac{Z}{|\boldsymbol{x}_i|}. \tag{2}$$

Here, c is the velocity of light ($c = 137.0373$ in a.u.) and $\boldsymbol{\alpha}$ and β' are 4×4 matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta' = \begin{pmatrix} 0 & 0 \\ 0 & -2I_2 \end{pmatrix}. \tag{3}$$

The vector $\boldsymbol{\sigma}$ has the 2×2 Pauli spin matrices as its components; the energy-scale has been shifted by $-c^2$ to subtract the electronic rest-energy.

In principle, some relativistic two-particle interactions neglected in (1) could be taken into account by using the Breit operator in 1st order perturbation theory [14]. For closed-shell systems the N-electron trial wavefunction Ψ is taken to be a single Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} |\psi_1(1)\psi_2(2)\cdots\psi_N(N)| \tag{4}$$

where the four-component Dirac orbitals ψ form an orthonormal set

$$\langle\psi_i, \psi_j\rangle = \sum_{\mu=1}^{4} \int d^3x\, \psi_i^{(\mu)*}\psi_j^{(\mu)} = \delta_{ij}. \tag{5}$$

Thus, the total energy is given by

$$E = \sum_i \langle\psi_i(1), h(1)\psi_i(1)\rangle + \frac{1}{2}\sum_i\sum_j \left\langle \psi_i(1)\psi_j(2), \frac{1-P_{ij}}{r_{12}}\psi_i(1)\psi_j(2)\right\rangle \tag{6}$$

where P_{ij} denotes the transposition operator. Now, it is convenient to partition ψ into two-component Pauli spinors φ and χ, the large and the small component, respectively,

$$\psi = \begin{pmatrix}\varphi\\ \chi\end{pmatrix}. \tag{7}$$

Substitution of (7) in (6) and application of the variational principle leads to the RHF equations (see e.g. [15]):

$$\begin{aligned} c\boldsymbol{\sigma}_1\boldsymbol{p}_1\chi_i(1) - \frac{Z}{|\boldsymbol{x}_1|}\varphi_i(1) + \sum_j \left\{\int d^3x_2\varphi_j^+(2)\frac{1-P_{ij}}{r_{12}}\varphi_j(2)\right.&\\ \left. + \int d^3x_2\chi_j^+(2)\frac{1-P_{ij}}{r_{12}}\chi_j(2)\right\}\varphi_i(1) &= \varepsilon_i\varphi_i(1) \end{aligned} \tag{8a}$$

$$\begin{aligned} c\boldsymbol{\sigma}_1\boldsymbol{p}_1\varphi_i(1) - \left\{\frac{Z}{|\boldsymbol{x}_1|} + 2c^2\right\}\chi_i(1)&\\ + \sum_j\left\{\int d^3x_2\varphi_j^+(2)\frac{1-P_{ij}}{r_{12}}\varphi_j(2) + \int d^3x_2\chi_j^+(2)\frac{1-P_{ij}}{r_{12}}\chi_j(2)\right\}\chi_i(1)&\\ = \varepsilon_i\chi_i(1).& \end{aligned} \tag{8b}$$

In order to reduce the size of the basis set to be used in the LCAO representation of the orbitals one would try to eliminate all the small components χ in either of the Eqs. (8); it is however not possible to accomplish this in an exact and closed way. Bersuker *et al.* [15] used the method of successive approximations to eliminate χ in (8a) and thus obtained an equation which is exact up to the order $(1/c)^2$ and which only involves the large components.

In the following a different approach is proposed. χ_i is assumed to be interconnected with φ_i by a fixed relation of the form

$$\chi_i = \Omega_i\varphi_i \tag{9a}$$

where

$$\Omega_i = \frac{1}{2c}B_i^{-1}\boldsymbol{\sigma}\boldsymbol{p} \tag{9b}$$

and

$$B_i = 1 + \frac{1}{2c^2}(e_i - \Phi). \tag{9c}$$

In (9) the function Φ represents a local potential and the parameters e_i are assumed to be real numbers. For a single electron in the field of a nucleus Eq. (9) holds exactly if Φ is identified with the nuclear potential and the e_i's are interpreted as the orbital energies (see later Eq. (21)) [14].

2.2. *Variational Equation for the Large Components*

With the above relation (9) the total energy (6) is given by

$$E = \sum_i \langle \varphi_i(1), \tilde{h}_i(1)\varphi_i(1)\rangle + \frac{1}{2}\sum_i \sum_j \langle \varphi_i(1)\varphi_j(2), \tilde{g}_{ij}(1, 2)\varphi_i(1)\varphi_j(2)\rangle \tag{10}$$

and the orthonormality condition (5) becomes

$$\langle \varphi_i, (1 + \Omega_i^+\Omega_j)\varphi_j\rangle = \delta_{ij}. \tag{11}$$

In Eq. (10) we used the abbreviations

$$\tilde{h}_i = -\frac{Z}{|\boldsymbol{x}|} + c\boldsymbol{\sigma p}\Omega_i + \Omega_i^+ c\boldsymbol{\sigma p} + \Omega_i^+\left(-\frac{Z}{|\boldsymbol{x}|} - 2c^2\right)\Omega_i \tag{12}$$

and

$$\begin{aligned}\tilde{g}_{ij}(1, 2) &= \frac{1 - P_{ij}}{r_{12}} + \Omega_i^+(1)\frac{1 - P_{ij}}{r_{12}}\Omega_i(1) + \Omega_j^+(2)\frac{1 - P_{ij}}{r_{12}}\Omega_j(2)\\ &\quad + \Omega_i^+(1)\Omega_j^+(2)\frac{1 - P_{ij}}{r_{12}}\Omega_j(2)\Omega_i(1) = \tilde{g}'_{12} + \tilde{g}''_{12}\end{aligned} \tag{13}$$

where the terms not containing P_{ij} were collected in $\tilde{g}'_{12}$ while those containing the transposition operator belong to $\tilde{g}''_{12}$.

In order to find a stationary energy value all the large components in the energy expression (10) are varied subject to the constraint of the orthonormality condition (11). In other words, the variations $\delta\chi$ which, according to the variational principle should be independent of the variations $\delta\varphi$ are compelled to have the form

$$\delta\chi = \Omega\,\delta\varphi. \tag{14}$$

Since all arguments concerning the diagonalization of the matrix of the Lagrange multipliers still hold, the eigenvalue equation

$$\left\{\tilde{h}_i(1) - \varepsilon_i\Omega_i^+(1)\Omega_i(1) + \sum_j \langle \varphi_j(2), \tilde{g}_{ij}(1, 2)\varphi_j(2)\rangle\right\}\varphi_i(1) \equiv \mathscr{F}_i\varphi_i(1) = \varepsilon_i\varphi_i(1) \tag{15}$$

and the total energy expression

$$E = \sum_i \varepsilon_i - \frac{1}{2}\sum_i \sum_j \langle \varphi_i(1)\varphi_j(2), \tilde{g}_{ij}(1, 2)\varphi_i(1)\varphi_j(2)\rangle \tag{16}$$

are finally obtained. The one-electron part in the l.h.s. of Eq. (15) is given explicitly by

$$\begin{aligned}\tilde{h}_i - \varepsilon_i\Omega_i^+\Omega_i \equiv D_i &= -\frac{Z}{|\boldsymbol{x}|} + \frac{1}{2}\boldsymbol{\sigma p}\frac{1}{B_i}\boldsymbol{\sigma p}\\ &\quad - \frac{1}{4c^2}\boldsymbol{\sigma p}\left\{(\varepsilon_i - e_i) + \left(\frac{Z}{|\boldsymbol{x}|} + \Phi\right)\right\}\frac{1}{B_i^2}\boldsymbol{\sigma p}.\end{aligned} \tag{17}$$

2.3 *Choice of Parameters*

The potential Φ and the parameters e_i were not obtained from the variational principle and thus have to be determined by some judiciously chosen criteria. Specific choices are the following: in a first approximation Φ is set equal to the potential of the bare nucleus

$$\Phi = -\frac{Z}{|\boldsymbol{x}|} \tag{18}$$

thus

$$B_i = B_i^{(0)}(e_i) \equiv B_i\left(e_i, -\frac{Z}{|\boldsymbol{x}|}\right). \tag{19}$$

This form of Φ has the advantage that after expansion of the radial parts of the φ_i into Slater-type functions all the one- and two-electron integrals appearing in Eq. (11) and (16) can be solved analytically (cf. the appendix).

Given X by (18), two choices for the parameters e_i have been tried:

a) $e_i = \varepsilon_i.$ (20)

If e_i is identified with the eigenvalue ε_i of Eq. (15), the operator D_i (17) is reduced to an operator $\tilde{d}_i$ well known from the elimination method [14] in the one-electron problem

$$\tilde{d}_i(\varepsilon_i) = -\frac{Z}{|\boldsymbol{x}|} + \frac{1}{2}\,\boldsymbol{\sigma p}\,\frac{1}{B_i^{(0)}(\varepsilon_i)}\,\boldsymbol{\sigma p}. \tag{21}$$

Furthermore, the eigenfunctions corresponding to different eigenvalues ε are guaranteed to be automatically orthogonal in the sense of (11) [16]. For this choice of parameters the quasi-relativistic equations for the spinor φ_i which have been derived by Bersuker *et al.* [15] may be obtained from (15) by substituting the power series expansion

$$B_i^{(0)}(\varepsilon_i)^{-1} \approx 1 - \frac{1}{2c^2}(\varepsilon_i - \Phi) + \cdots$$

and neglecting all terms of order higher than $O(1/c^2)$. The resulting equation agrees with the quasi-relativistic HF equation (Eq. (11) in [15]).

b) $e_i = d_i \equiv \langle \varphi_i, \tilde{d}_i(e_i)\varphi_i\rangle / \langle \varphi_i, \varphi_i\rangle = \langle \varphi_i, \tilde{h}_i(e_i)\varphi_i\rangle.$ (22)

If e_i is identified with the expectation value of the one-electron operator $\tilde{d}_i(e_i)$, the numerical solution of Eq. (15) is simplified, since the two-electron contributions do no longer depend on the eigenvalues ε to be determined. However, for the choice (22) Eq. (15) satisfies the variational principle only approximately since in deriving (15) the Ω_i have been assumed to be independent of the wavefunctions.[1]

---

[1] This point has been noted by the referee.

2.4. Formulae for Matrix Elements

In a central field the orbitals ψ can be separated by using polar coordinates [17]

$$\psi(x) = \psi_{n\kappa\mu}(r, \vartheta, \varphi) = \frac{1}{r}\begin{Bmatrix} P_{n\kappa}(r)\chi_{\kappa\mu}(\vartheta, \varphi) \\ iQ_{n\kappa}(r)\chi_{-\kappa\mu}(\vartheta, \varphi) \end{Bmatrix} \tag{23}$$

with the phase chosen in such a way that the radial functions P and Q are both real. Properties of the complete and orthonormal set of spinors χ are given in [17]. The quantum numbers κ and μ are interrelated with the total angular momentum j and the orbital angular momentum l by

$$j = |\kappa| - \frac{1}{2}$$

$$l = j + \frac{1}{2}\frac{\kappa}{|\kappa|}$$

and $\mu = -j, -j + 1, \ldots, j - 1, j$. The principal quantum number n labels orbitals which cannot be distinguished by κ and μ. Using

$$\boldsymbol{\sigma p} f(r) \boldsymbol{\sigma p}\frac{P(r)}{r} = \frac{1}{r}\left\{f\left(-P'' + \frac{l(l+1)}{r^2}P\right) - f'\left(P' + \frac{\kappa}{r}P\right)\right\} \tag{24}$$

where the prime denotes differentiation with respect to r, one obtains

$$\begin{aligned} \langle\varphi_i, \tilde{d}_i(e_i)\varphi_i\rangle = \int_0^\infty dr\bigg\{-\frac{Z}{r}P^2 + \frac{1}{2B}\bigg[-PP'' + \frac{l(l+1)}{r^2}P^2 \\ - \frac{1}{2c^2}\frac{Z}{Br^2}\left(PP' + \frac{\kappa}{r}P^2\right)\bigg]\bigg\} \end{aligned} \tag{25}$$

with $P \equiv P_{n_i\kappa_i}$ and $B \equiv B_i^{(0)}(e_i)$. The orthonormality condition (11) results in

$$\begin{aligned} \int_0^\infty dr\bigg\{P_iP_j + \frac{1}{4c^2}\frac{1}{B_iB_j}\bigg[-P_iP_j'' + \frac{l_j(l_j+1)}{r^2}P_iP_j \\ - \frac{1}{2c^2}\frac{B_i + B_j}{B_iB_j}\frac{Z}{r^2}\left(P_iP_j' + \frac{\kappa_j}{r}P_iP_j\right)\bigg]\bigg\} = \delta_{ij}. \end{aligned} \tag{26}$$

The two-electron part of Eq. (16) can be evaluated along the lines given by Grant [1]. The Coulomb integrals are given by

$$\langle\varphi_i(1)\varphi_j(2), \tilde{g}'_{12}\varphi_i(1)\varphi_j(2)\rangle = \sum_\nu a_\nu((j, \mu)_i, (j, \mu)_j)F_\nu(i, j)$$

where

$$\nu = 0, 2, 4, \ldots, \qquad \mathrm{Min}\,[(2j_i - 1), (2j_j - 1)] \tag{27}$$

and the exchange integrals are given by

$$\langle\varphi_i(1)\varphi_j(2), \tilde{g}''_{12}\varphi_j(1)\varphi_i(2)\rangle = \sum_\nu b_\nu((j, \mu)_i, (j, \mu)_j)G_\nu(i, j)$$

where

$$|j_i - j_j| \leqslant \nu \leqslant j_i + j_j \quad \text{and} \quad j_i + j_j + \nu = \begin{cases} \text{even if } \dfrac{\kappa_i}{|\kappa_i|} \neq \dfrac{\kappa_j}{|\kappa_j|} \\ \text{odd if } \dfrac{\kappa_i}{|\kappa_i|} = \dfrac{\kappa_j}{|\kappa_j|} \end{cases}. \tag{28}$$

Therein the notations

$$F_\nu(i, j) = \int_0^\infty dr_1\, dr_2 U_\nu(1, 2)\{P_i^2(r_1) + Q_i^2(r_1)\} \times \{P_j^2(r_2) + Q_j^2(r_2)\} \tag{29}$$

$$G_\nu(i, j) = \int_0^\infty dr_1\, dr_2 U_\nu(1, 2)\{P_i(r_1)P_j(r_1) + Q_i(r_1)Q_j(r_1)\} \times \{P_i(r_2)P_j(r_2) + Q_i(r_2)Q_j(r_2)\} \tag{30}$$

with

$$Q_i = \frac{1}{2c}\frac{1}{B_i^{(0)}}\left(P_i' + \frac{\kappa}{r}P_i\right) \tag{31}$$

and

$$U_\nu(1, 2) = r_<^\nu / r_>^{\nu+1}$$

are used. The numbers a_ν and b_ν can be taken from tables [1].

3. Calculations Using a Minimum Basis Set of Slater-Type Functions

The radial functions P are expanded according to

$$P_{n\kappa}(r) = \sum_{i=1}^{n-l} c_i r^{n_i} \exp\{-\zeta_i r\}. \tag{32}$$

The exponents ζ are real nonlinear variational parameters. Given ζ, the coefficients c_i are completely determined via the orthonormality condition (26). All exponents n_i are taken to be integers $n_i = l + i$, though the cusp condition for Eq. (15) requires noninteger values $n' = [\kappa^2 - (Z/c)^2]^{1/2}$.

Actually, because of relation (31) the radial part Q of the small component is expanded into a definite infinite set of STFs; this becomes evident if the function B^{-1} is expanded as a power-series of r.

The orbital exponents ζ which yield a stationary value for the total energy (16) have been determined for the atoms He, Be, Ne, Mg, Ar, Kr, Xe and for the ion Cu$^+$. Optimal values ζ were calculated iteratively: in the kth cycle each exponent ζ_i was varied by small amounts $\mp \delta_i$ and corrected afterwards according to

$$\zeta_i^{(k+1)} = \zeta_i^{(k)} + wT_i^{(k)} \tag{33}$$

with a damping factor $w \leqslant 1$ and

$$T_i = -\frac{\delta_i}{2}[E(\zeta + \delta_i) - E(\zeta - \delta_i)]/[E(\zeta + \delta_i) + E(\zeta - \delta_i) - 2E(\zeta)]. \tag{34}$$

Convergence was assumed if all quotients $|T_i|$ became less than a threshold value 0.05 for Xe and 0.0001 for all other atoms.

The total relativistic energies E_{RSZ} are recorded in Table 1. Energies calculated according to both choices of parameters e_i (i.e. $e_i = \varepsilon_i$ and $e_i = d_i$) are almost equal for low atomic numbers but differ increasingly for heavier atoms in such a way that the values for $e_i = \varepsilon_i$ become lower than those for the second choice of e_i. The MBS energies are less negative than the energies E_{RHF} calculated by the numerical RHF method [8]. Values for the percentage error $100(E_{\mathrm{RHF}} - E_{\mathrm{RSZ}})/E_{\mathrm{RHF}}$ range from 0.11% to 0.58% and show strong scattering for different atoms. However, the differences ΔE_{RSZ} between relativistic (using $e_i = \varepsilon_i$) and nonrelativistic [18, 19] single-ζ total energies follow closely the corresponding energy differences ΔE_{RHF} of numerical RHF and NRHF [20] calculations (see columns 1 and 2 of Table 2); the values ΔE_{RSZ} and ΔE_{RHF} agree within less than 7%.

In the calculation of $\Delta E_{\mathrm{RSZ}} = E_{\mathrm{RSZ}} - E_{\mathrm{NRSZ}}$ both total energies have been optimized with respect to the orbital exponents ζ. If the exponents of NRHF single-ζ wavefunctions are used to calculate E_{RSZ}, relativistic corrections $\Delta E^{(1)}_{\mathrm{RSZ}}$ result which are shown in column 3 of Table 2. For low atomic numbers both ΔE values almost agree, but with increasing Z, $\Delta E^{(1)}_{\mathrm{RSZ}}$ becomes progressively smaller compared to ΔE_{RSZ}. Relativistic corrections approximately comparable to $\Delta E^{(1)}_{\mathrm{RSZ}}$ have been obtained by Hartmann and Clementi [21] who calculated relativistic first-order perturbation energies $\Delta E^{(1)}_{\mathrm{H\text{-}Cl}}$ using NRHF single-ζ wavefunctions and a

Table 1. Total relativistic energies [negative values in a.u.]

Atom	Z	e[a]	E_{RSZ}[b]	E_{RHF}[c]	Error[d]
He	2	ε d	2.847764	2.8618	0.49
Be	4	ε d	14.5594	14.5759	0.11
Ne	10	ε d	127.9494	128.6920	0.58
Mg	12	ε d	199.1638 199.1637	199.9352	0.39
Ar	18	ε d	527.5733 527.5727	528.6845	0.21
Kr	36	ε d	2779.9115 2779.8929	2788.8845	0.32
Xe	54	ε d	7420.0079 7419.8719	7447.1605	0.37
Cu^+	29	ε d	1646.2005 1646.1948	1653.2211	0.42

[a] Parameter e chosen according to Eq. (20) ($e = \varepsilon$) or Eq. (22) ($e = d$).

[b] Relativistic single-ζ calculation.

[c] Calculated by means of Desclaux's program [7].

[d] Percentage error $100(E_{\mathrm{RHF}} - E_{\mathrm{RSZ}})/E_{\mathrm{RHF}}$.

Table 2. Total relativistic energy corrections (negative values in a.u.)

Atom	Z	ΔE_{RSZ}[a]	ΔE_{RHF}[b]	$\Delta E^{(1)}_{\mathrm{RSZ}}$[a,c]	$\Delta E^{(1)}_{\mathrm{H-CI}}$[d]	E_{mag}[e]
He	2	0.000108	0.000133	0.000108	0.000004	0.00006
Be	4	0.0027	0.0029	0.0027	0.0015	0.0007
Ne	10	0.1373	0.1449	0.1365	0.1152	0.0175
Mg	12	0.3060	0.3205	0.3038	0.2671	0.0339
Ar	18	1.8080	1.8670	1.7781	1.6822	0.1434
Kr	36	35.392	36.830	33.175		
Xe	54	200.2	215.022	174.156		
Cu^+	29	14.046	14.493[f]	13.457		

[a] Difference between relativistic ($e = \varepsilon$; Eq. (20)) and NRHF [18, 19] single-ζ total energy.
[b] Difference between numerical RHF and NRHF [20] total energy.
[c] Relativistic energy calculated using the exponents of NRHF single-ζ wavefunctions.
[d] First order perturbation energy using the Breit operator in Pauli approximation and NRHF single-ζ wavefunctions [21].
[e] Magnetic interaction calculated by means of Desclaux's program [7].
[f] NRHF energy calculated by means of Desclaux's program [7] setting $c = 137 \cdot 10^6$.

part of the Breit operator in the Pauli approximation (column 4 of Table 2). Since the values $\Delta E^{(1)}_{\mathrm{H-CI}}$ include relativistic effects in the two-electron interaction, the magnetic contribution E_{mag} calculated by Desclaux's numerical RHF program [7] is listed in the last column of Table 2. Taking into account these contributions the values of $\Delta E^{(1)}_{\mathrm{RSZ}}$ and $\Delta E^{(1)}_{\mathrm{H-CI}}$ are similar except for He and Be.

Table 3 contains orbital energies ε for Kr obtained from (15) by solving the implicit equation $\langle \varphi_i, \mathscr{F}_i \varphi_i \rangle = \varepsilon_i \langle \varphi_i, \varphi_i \rangle$ with $\Phi = -Z/|x|$. For either choice of the parameters the values ε are in general agreement with experimental X-ray level data as well as with the eigenvalues of numerical RHF calculations; the largest deviations are found for the energetically highest orbitals. The fine structure splitting $\Delta\varepsilon = \varepsilon_{n,1-1/2} - \varepsilon_{n,1+1/2}$ is in fairly good agreement with experimental data.

Except for the case of the ion Cu^+ ($3d^{10}$) where the limitations of an MBS become apparent, the results for Kr are representative for all other atoms under consideration. For the Cu^+ ion (Table 4) the lowest orbital energies agree reasonably well with experimental binding energies for metallic Cu [23], but the highest-lying d-orbitals are destabilized to such an extent that they become antibonding. This deficiency is due to the use of an MBS only. It also appears in the corresponding nonrelativistic calculation and can be avoided by taking a $3d$-function of double-ζ quality.

Table 5 shows the optimized exponents ζ of the relativistic MBS-STFs and relativistic screening constants σ which are defined as the differences between the RHF and the NRHF [18, 19] orbital exponents. The values ζ_{1s} increase rapidly with increasing atomic number. From Cu^+ on they even exceed Z, indicating a deshielding of the nucleus. In contrast, the shielding ($Z - \zeta_{1s}$) of the nonrelativistic $1s$-function becomes larger for high Z]18, 19]. The reason for the strong contraction of the relativistic $1s$-orbitals is discussed later.

Table 3. Orbital energies ε for Kr (negative values in a.u.)

Shell	j	$\varepsilon_{\mathrm{RSZ}}$ [a]	$\varepsilon_{\mathrm{RSZ}}$ [b]	$\varepsilon_{\mathrm{NRSZ}}$ [c]	$\Delta\varepsilon$ [a,d]	$\varepsilon_{\mathrm{RHF}}$ [e]	$\Delta\varepsilon$ [e,d]	E_{exp} [f]	$\Delta\varepsilon$ [f,d]
1*s*	1/2	528.943	528.709	520.068		529.695		526.47	
2*s*	1/2	71.226	71.070	68.717		72.081		70.60	
2*p*	1/2	64.297	64.120			64.875		63.47	
				62.625	1.820		1.996		1.92
2*p*	3/2	62.477	62.303			62.879		61.55	
3*s*	1/2	10.736	10.653	10.133		11.225		10.6	
3*p*	1/2	8.323	8.250			8.620		8.18	
				7.877	0.319		0.307		0.32
3*p*	3/2	8.004	7.931			8.313		7.86	
4*s*	1/2	1.066	1.051	1.007		1.188		1.012	
4*p*	1/2	0.456	0.444			0.5415		0.539	
				0.4209	0.024		0.0272		0.025
4*p*	3/2	0.432	0.420			0.5143		0.514	
3*d*	3/2	2.948	2.869			3.778			
				2.943	0.042		0.051	3.27	
3*d*	5/2	2.906	2.828			3.727			

[a] Calculated with $e = \varepsilon$ (Eq. (20)).
[b] Calculated with $e = d$ (Eq. (22)).
[c] Calculated by the technique of Roothaan–Bagus [28].
[d] $\Delta\varepsilon = \varepsilon_{n,1-1/2} - \varepsilon_{n,1+1/2}$.
[e] Calculated by means of Desclaux's program [7].
[f] X-ray levels from Ref. [22].

Table 4. Orbital energies ε for Cu$^+(3d^{10})$ (negative values in a.u.)

Shell	j	$\varepsilon_{\mathrm{RSZ}}$ [a]	$\varepsilon_{\mathrm{NRSZ}}$ [b]	$\Delta\varepsilon$ [c]	$\varepsilon_{\mathrm{RFH}}$ [d]	$\Delta\varepsilon$ [c]	E_{exp} [e]
1*s*	1/2	332.610	328.926		332.55		330.14
2*s*	1/2	41.302	40.262		41.958		40.48
2*p*	1/2	36.163			36.559		35.11
			35.514	0.703		0.721	
2*p*	3/2	35.460			35.838		34.38
3*s*	1/2	4.769	4.523		5.471		4.57
3*p*	1/2	3.177			3.743		
			2.971	0.110		0.096	2.87
3*p*	3/2	3.067			3.647		
3*d*	3/2	−0.177			0.810		
			−0.208	0.017		0.012	
3*d*	5/2	−0.194			0.798		

[a] Calculated with $e = \varepsilon$ (Eq. (20)).
[b] Calculated by the technique of Roothaan–Bagus [28].
[c] $\Delta\varepsilon = \varepsilon_{n,1-1/2} - \varepsilon_{n,1+1/2}$.
[d] Ref. [3]; a finite nucleus is assumed.
[e] Values for metallic Cu as quoted in [23].

Table 5. Orbital exponents ζ^{a} of relativistic minimum basis set Slater-type functions and relativistic screening corrections σ^{b}

Atom	Z		$1s$	$2s$	$2p_{1/2}$	$2p_{2/3}$	$3s$	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
He	2	ζ	1.68764								
		σ	0.0001								
Be	4	ζ	3.6862	0.9562							
		σ	0.0014	0.0002							
Ne	10	ζ	9.6683	2.8855	2.8847	2.8770					
		σ	0.0262	0.0063	0.0055	−0.0022					
Mg	12	ζ	11.6556	3.7071	3.9230	3.9108	1.1044				
		σ	0.0467	0.0111	0.0101	−0.0021	0.0019				
Ar	18	ζ	17.6741	6.1581	7.0518	7.0053	2.5972	2.2639	2.2515		
		σ	0.1666	0.0429	0.0477	0.0012	0.0116	0.0092	−0.0032		
Kr	36	ζ	36.6478	13.6160	16.5533	16.0971	7.1439	6.9269	6.8124	6.8560	6.8098
		σ	1.4132	0.4170	0.5298	0.0736	0.1330	0.1155	0.0014	−0.0193	−0.0655
Xe	54	ζ	57.9735	21.5273	27.0582	25.3160	12.3102	12.3624	11.9739	13.3847	13.2087
		σ	5.0520	1.6258	2.1409	0.3987	0.4514	0.4732	0.0847	0.0691	−0.1069
Cu^{+}	29	ζ	29.0608	10.7292	12.8017	12.5784	5.2237	4.9463	4.8785	4.2091	4.1235
		σ	0.7290	0.1958	0.2480	0.0247	0.0751	0.0682	0.0004	0.0058	−0.0798

Atom	Z		$4s$	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$	$5s$	$5p_{1/2}$	$5p_{3/2}$
Kr	36	ζ	2.8656	2.4655	2.4150					
		σ	0.0367	0.0232	−0.0273					
Xe	54	ζ	6.7609	6.4270	6.2236	5.4257	5.3389	2.9162	2.5181	2.4869
		σ	0.2177	0.1877	−0.0157	−0.0476	−0.1344	0.0726	0.0333	−0.0258

[a] Calculated with $e = \varepsilon$ (Eq. (20)).

[b] $\sigma = \zeta_{RSZ} - \zeta_{NRSZ}$.

As one would expect, for a given atom the relativistic screening constants σ decrease whenever the quantum numbers n and j are raised. In comparison to NRHF calculations some of the highest lying RHF orbitals are deshielded. This is due to an indirect relativistic effect [24–26]. As a consequence of the relativistic contraction of the inner shells the nuclear charge for the outermost orbitals is screened to a larger amount than in the case of nonrelativistic atoms.

The radial exponents n of the MBS functions (32) were chosen to be integers. In the following, the capability of these functions to account for the relativistic modifications of the shape of the radial wavefunctions is discussed. Since relativistic effects are largest for the innermost orbitals as judged from the screening constants σ, the 1s-function is taken as an example.

Table 6 shows the relativistic mean radii and the ratios of their relativistic and nonrelativistic values for the 1s-orbitals; these quantities are given for the numerical and the analytical single-ζ RHF wavefunctions as well. The mean radii $\bar{r}_{\mathrm{RSZ}}$ differ from $\bar{r}_{\mathrm{RHF}}$ within 1–4%, the largest deviation occurring for He. However, if Z increases the ratios f_{RSZ} decrease more rapidly than the ratios f_{RHF}. The reason for the excessive contraction of the MBS 1s-orbitals can be inferred by fitting the numerical RHF and NHRF functions by a single STF of the form $r^{\gamma} e^{-\zeta r}$, where ζ is considered as fitting parameter in the least-squares procedure. First γ is fixed by $\gamma = 1$ for both functions. In a second step γ for the relativistic function is set equal to the value for the hydrogenic Dirac 1s-orbital, $\gamma = [1 - (Z/c)^2]^{1/2}$. The values of ζ and the RMS errors are given in Table 7.

In the nonrelativistic case the expected result $\zeta < Z$ is obtained. However, in the relativistic case the exponents ζ exceed Z if $\gamma = 1$. Furthermore the RMS errors grow strongly for atoms with higher atomic numbers. But, if γ is chosen to satisfy the cusp condition the relation $\zeta < Z$ is fulfilled again and the RMS errors are reduced to those for the nonrelativistic functions.

Table 6. Mean radii $\bar{r}$ and ratios f of the relativistic and nonrelativistic mean radii of 1s-orbitals

Atom	Z	$\bar{r}_{\mathrm{RSZ}}$[a]	$\bar{r}_{\mathrm{RHF}}$[b]	f_{RSZ}[c]	f_{RHF}[d]
He	2	0.8888	0.9272	0.9999	0.9999
Be	4	0.4069	0.4149	0.9936	0.9998
Ne	10	0.1552	0.1574	0.9913	0.9983
Mg	12	0.1287	0.1303	0.9899	0.9976
Ar	18	0.08487	0.08562	0.9858	0.9944
Kr	36	0.04094	0.04147	0.9610	0.9771
Xe	54	0.02592	0.02665	0.9146	0.9470

[a] Calculated with $e = \varepsilon$ (Eq. (20)).

[b] Calculated by means of Desclaux's program [7].

[c] Nonrelativistic values calculated by the technique of Roothaan-Bagus [28].

[d] Nonrelativistic values from Ref. [20].

Table 7. Orbital exponents ζ and RMS errors $F(\times 10^4)$ obtained by fitting the nonrelativistic[a] and the relativistic[b] 1*s*-orbitals to $r^{\gamma}e^{-\zeta r}$

		$(1s)_{nr}$		$(1s)_r$			
		$\gamma = 1$		$\gamma = 1$		$\gamma = (1 - (Z/c)^2)^{1/2}$	
Atom	Z	ζ	F	ζ	F	ζ	F
He	2	1.6883	157	1.6885	123	1.6883	123
Be	4	3.682	106	3.684	107	3.682	106
Ne	10	9.619	97	9.643	105	9.617	96
Mg	12	11.599	97	11.641	110	11.597	96
Ar	18	17.554	93	17.702	133	17.549	93
Kr	36	35.499	77	36.761	342	35.473	75
Xe	54	53.470	68	58.077	876	53.403	65
Hg	80	79.488	59	97.345	2590	79.258	57

[a] Wave functions calculated by means of Desclaux's program [7] setting $c = 137\cdot 10^6$.

[b] Wave functions calculated by means of Desclaux's program [7].

4. Conclusion

The presented MBS results are affected by two approximations:

a) the fixed relationship (9) between large and small component,
b) the use of integer principal quantum numbers n in the basis functions.

The fairly good agreement for total relativistic energy-corrections and orbital energies with the results of numerical RHF calculations indicates that approximation a) does not introduce large errors, at least not for atoms up to atomic number 54 (Xe). Different choices of the parameters e in (9) yield only slightly different numerical results. On the other hand, consideration of orbital exponents and mean radii shows that the restriction of n to integer values is acceptable for low atomic numbers only. For $Z > 36$ only an MBS of STFs with noninteger radial exponents n is flexible enough to account for the relativistic contraction and deformation of the radial wavefunctions.

Acknowledgement. The authors wish to express their gratitude to Professors O. E. Polansky and P. Schuster for their continuous interest. We thank Miss E. Wechsel for her skillful help in developing and testing the computer programs. We are grateful to Dr. P. Hafner for providing us with a copy of Desclaux's program and to H. Gruen for reading the English manuscript.

Appendix

All the one- and two-electron integrals referred to can be reduced to known elementary integrals and can be calculated by recurrence relations.

A.1. The One-Electron Integrals

If the functions P are expanded according to (32), all the integrals appearing in Eqs. (25) and (26) are of the form

$$S(m, n; \eta, a) = \int_0^\infty dx \frac{e^{-\eta x} x^m}{(a + x)^n} \quad \begin{matrix} m \geqslant 0 \\ n \geqslant 0 \end{matrix} \tag{A1}$$

since

$$\int_0^\infty dr\, e^{-\eta r} r^m B^{-n} = \left[1 + \frac{1}{2c^2}\right]^{-n} S(m + n, n; \eta, a)$$

with

$$B = 1 + \frac{1}{2c^2}\left(e + \frac{Z}{r}\right) \quad \text{and} \quad a = Z/(2c^2 + e).$$

The integrals $S(m, n)$ (the arguments η and a are omitted for the sake of simplicity) can be calculated recursively according to

$$S(m, n + 1) = \frac{1}{n}\left\{\frac{\delta_{m0}}{a^n} - \eta S(m, n) + m S(m - 1, n)\right\} \tag{A2}$$

$$S(m + 1, 1) = \frac{m!}{\eta^{m+1}} - a S(m, 1) \tag{A3}$$

starting from

$$S(m, 0) = \frac{m!}{\eta^{m+1}} \tag{A4}$$

$$S(0, 1) = e^{\eta a} E_1(\eta a). \tag{A5}$$

For $m = 0$ the last term in the recurrence relation (A2) has to be omitted. The exponential integral E_1 is defined by (A20) (see Sect. A.2.).

A.2 The Two-Electron Integrals

All integrals appearing in Eqs. (29) and (30) have the basic form

$$I^\nu(M, N; \eta, \xi; i, m; j, n) = \iint_0^\infty dr_1\, dr_2 U_\nu(1, 2) \\ \times r_1^M r_2^N\, e^{-\eta r_1}\, e^{-\xi r_2} (2c^2)^{-m-n} B_i^{-m}(r_1) B_j^{-n}(r_2) \tag{A6}$$

where

$$B_i(r_1) = 1 + \frac{1}{2c^2}(e_i + Z/r_1);$$

$B_j(r_2)$ is given analogously. The above integrals I^ν are rewritten

$$I^\nu = (2c^2 + e_i)^{-m}(2c^2 + e_j)^{-n} \\ \times \{J(N + n + \nu, M + m - \nu - 1; \xi, \eta; j, n; i, m) \\ + J(M + m + \nu, N + n - \nu - 1; \eta, \xi; i, m; j, n)\} \tag{A7}$$

with

$$J(n, m; \eta, \xi; a, p; b, q) = \int_0^\infty dv \frac{e^{-\eta v} v^n}{(a + v)^p} \int_v^\infty du \frac{e^{-\xi u} u^m}{(b + u)^q} \tag{A8}$$

where $a = Z/(2c^2 + e_i)$ and $b = Z/(2c^2 + e_j)$. In order to simplify the notation, the abbreviation $J(n, m; \eta, \xi; a, p; b, q) \equiv J(n, p; m, q)$ will be used.

Integrating by parts one gets the following recurrence relations from (A8)

$$\begin{aligned} J(n, p; m, q + 1) = \frac{1}{q}\{&-\xi J(n, p; m, q) + mJ(n, p; m - 1, q) \\ &+ U(n + m, p, q)\} \quad q \geqslant 1, m \geqslant 0 \end{aligned} \tag{A9}$$

$$J(n, p; m, 0) = \frac{1}{\xi}\{U(n + m, p, 0) + mJ(n, p; m - 1, 0)\} \tag{A10}$$

$$\begin{aligned} J(n, p + 1; m, q) = \frac{1}{p}\Big\{&-\eta J(n, p; m, q) + nJ(n - 1, p; m, q) \\ &- U(n + m, p, q) + \frac{\delta_{n0}}{a^p} S(m, q)\Big\} \quad p \geqslant 1, n \geqslant 0 \end{aligned} \tag{A11}$$

$$J(n, 0; m, q) = \frac{1}{\eta}\{-U(n + m, 0, q) + nJ(n - 1, 0; m, q) + \delta_{n0} S(m, q)\}. \tag{A12}$$

Here, in addition to $S(m, n) \equiv S(m, n; (\eta + \xi), b)$ defined by (A1), a further auxiliary integral

$$U(n, p, q) = \int_0^\infty e^{-(\xi + \eta)v}(a + v)^{-p}(b + v)^{-q} v^n \, dv \tag{A13}$$

has been introduced. For $n \geqslant 0$ and $p, q \geqslant 1$, U can be recurred by the relation

$$U(n, p, q) = \frac{1}{a - b}\{U(n, p - 1, q) - U(n, p, q - 1)\}. \tag{A14}$$

If one or both of the indices p or q are zero, U reduces to S.

In order to start the recurrence calculation of $J(n, p; m, q)$ one needs

$$J(0, 0; 0, 0) = \frac{1}{\xi} \frac{1}{\xi + \eta} \tag{A15}$$

$$J(0, 1; 0, 0) = \frac{1}{\xi} U(0, 1, 0) \tag{A16}$$

$$J(0, 0; 0, 1) = \frac{1}{\eta}\{e^{\xi b} E_1(\xi b) - S(0, 1)\} \tag{A17}$$

and furthermore $J(0, 1; 0, 1)$. This integral

$$J(0, 1; 0, 1) = \int_0^\infty dv \frac{e^{-\eta v}}{(a + v)} \int_v^\infty du \frac{e^{-\xi u}}{(b + u)} \tag{A18}$$

can be reduced to a sum of single integrals of the form

$$\int_\kappa^\infty dt\,\frac{e^{-t}}{t}\ln S_i(t)$$

by changing the variables according to

$$t = \eta(a + v) + \xi(b + u) \quad \text{and} \quad x = (\xi u + \xi b)/t.$$

Expanding the functions $\ln S_i(t)$ into appropriate convergent series and integrating, one obtains the formula

$$J(0, 1; 0, 1) = e^\kappa\Bigg(E_1(\kappa)\ln(\kappa/a\eta) + E_1^{(2)}(\kappa) - \sum_i^\infty \frac{1}{i}\left\{\left(\frac{a\eta}{\kappa}\right)^i E_{i+1}(\kappa) - \frac{1}{(\xi+\eta)^i} \times [\eta^i H(i+1, i; \kappa, -\xi\delta) - \xi^i H(i+1, i; \kappa, \eta\delta)]\right\}\Bigg) \tag{A19}$$

where $\kappa = \eta a + \xi b$ and $\delta = b - a$. The ith exponential integral E_i is defined by (see e.g. [27])

$$E_i(x) = \int_x^\infty e^{-t}\frac{1}{t^i}\,dt \quad x > 0 \tag{A20}$$

and satisfies the recurrence relation

$$E_{i+1}(x) = \frac{1}{i}\left(\frac{e^{-x}}{x^i} - E_i(x)\right). \tag{A21}$$

The auxiliary integral

$$H(i, j; \kappa, \mu) = \int_\kappa^\infty \frac{e^{-t}}{t^i}(t + \mu)^j\,dt \tag{A22}$$

can be recurred according to

$$H(i, j) = H(i - 1, j - 1) + \mu H(i, j - 1) \tag{A23}$$

(the arguments κ and μ are omitted) together with (A21). $E_1^{(2)}$ is given by [27]

$$E_1^{(2)}(x) = \int_x^\infty dt\,\frac{E_1}{t}(t) = \tfrac{1}{2}(\ln x + C)^2 + \frac{\pi^2}{12} + \sum_{i=1}^\infty (-1)^i \frac{x^i}{i^2 i!} \tag{A24}$$

where C is Catalan's constant.

References

1. Grant, I. P.: Advan. Phys. **19**, 747 (1970)
2. Coulthard, M. A.: Proc. Phys. Soc. **91**, 44 (1967)
3. Smith, F. C., Johnson, W. R.: Phys. Rev. **160**, 136 (1967)
4. Mann, J. B., Waber, J. T.: J. Chem. Phys. **53**, 2397 (1970)
5. Libermann, D. A., Cromer, D. T., Waber, J. T.: Comp. Phys. Commun. **2**, 107 (1971)
6. Desclaux, J. P., Mayers, D. F., O'Brien, F.: J. Phys. B. **4**, 631 (1971)

7. Desclaux, J. P.: Comp. Phys. Commun. **9**, 31 (1975)
8. Malý, J., Hussonnois, M.: Theoret. Chim. Acta (Berl.) **28**, 363 (1973)
9. Malý, J., Hussonnois, M.: Theoret. Chim. Acta (Berl.) **31**, 137 (1973)
10. Desclaux, J. P.: At. Data Nucl. Data Tables **12**, 311 (1973)
11. Kim, Y.-K.: Phys. Rev. **154**, 17 (1967)
12. Leclercq, J. M.: Phys. Rev. A**1**, 1358 (1970)
13. Kagawa, T.: Phys. Rev. A**12**, 2245 (1975)
14. Bethe, H. A., Salpeter, E. E.: Quantum mechanics of one- and two-electron atoms. Berlin: Springer 1957
15. Bersuker, I. B., Budnikov, S. S., Leizerov, B. A.: Intern. J. Quantum Chem. **6**, 849 (1972)
16. Rosicky, F., Weinberger, P., Mark, F.: J. Phys. B. **9**, 2971 (1976)
17. Rose, M. E.: Relativistic electron theory. New York: Wiley 1961
18. Clementi, E., Raimondi, D. L.: J. Chem. Phys. **38**, 2686 (1963)
19. Clementi, E., Raimondi, D. L., Reinhardt, W. P.: J. Chem. Phys. **47**, 1300 (1967)
20. Froese Fischer, C.: The Hartree–Fock method for atoms. New York: Wiley 1977
21. Hartmann, H., Clementi, E.: Phys. Rev. **133**A, 1295 (1964)
22. Bearden, J. A., Burr, A. F.: Rev. Mod. Phys. **39**, 125 (1967)
23. Rosen, A., Lindgren, I.: Phys. Rev. **176**, 114 (1968)
24. Desclaux, J. P.: Intern. Quantum Chem. Symp. **6**, 25 (1972)
25. Desclaux, J. P., Kim, Y.-K.: J. Phys. B. **8**, 1177 (1975)
26. Rose, S. J., Grant, I. P., Pyper, N. C.: J. Phys. B. **11**, 1171 (1978)
27. Kourganoff, V.: Basic methods in transfer problems. Oxford: Clarendon 1952
28. Roothaan, C. C. J., Bagus, P. S.: Methods Comp. Phys. **2**, 47 (1963)

Received April 4, 1979/August 23, 1979