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Relativistic electronic-structure calculations employing a two-component no-pair formalism with external-field projection operators

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A no-pair formalism employing external-field projection operators correct to second order in the potential is used to calculate the $1s$ energies of one-electron atoms and ground-state properties of the bromine and silver atoms in the framework of the multireference double-excitation configuration-interaction (MRD-CI) method. It is found that the relativistic two-component method that has been used reproduces the one-particle energies of the Dirac equation to order $(Z\alpha)^3$. The operator is bounded from below and can be used variationally in relativistic electron-structure calculations of many-electron atoms and molecules. The relativistic correction to the total energy recovers 97% of the relativistic correction of the Dirac-Hartree-Fock (DHF) result in the case of the bromine atom and more than 99% in the case of the silver atom. The relativistic correction of the ionization potential of silver has been calculated to be 0.47 eV at the CI level, in good agreement with DHF results, the correlation contribution in the relativistic case being 0.42 eV. The remaining discrepancy of the absolute value of 6.85 eV (DHF 6.34 eV) to experiment (7.57 eV) is attributed to basis-set deficiencies. The corresponding CI value of the electron affinity (relativistic CI value 1.05 eV, nonrelativistic 0.90 eV) is in much better agreement with experiment (1.30 eV). It is found that correlation contribution and relativistic effects are nonadditive.

I. INTRODUCTION

It has recently been proposed to employ the operators of the no-pair equation with free particle projection operators[1–3] for practical calculations of the electronic structure of atoms and molecules in order to enable a calculation of relativistic effects in the framework of a theory which enjoys the advantage of being derived from first principles and yet can be efficiently used in connection with existing computer programs for treating multiparticle interactions by virtue of a formulation in terms of two-component wave functions in configuration space, thus decoupling electron and positron degrees of freedom. First calculations on one- and two-electron systems[4–6] as well as self-consistent field (SCF) and configuration-interaction (CI) calculations on a multielectron atom[6] yielded encouraging results, although a careful analysis[4] shows that the binding energy of one-electron atoms as obtained from the no-pair equation with free-particle projection operators is in disagreement with Dirac equation results by a term of order $(Z\alpha)^3$.

This discrepancy in turn leads to an overestimation of the relativistic correction to the total energy of about 20% in the case of the bromine atom or about 0.2% of the total energy itself,[6] compared with Dirac-Hartree-Fock (DHF) calculations.[7] These results seem to be quite acceptable, especially since the value of the total energy is only of secondary importance when considering excitations in the valence shells in an *ab initio* calculation of the electronic spectrum of the system under investigation.

Earlier theoretical work[3] suggested, however, that a Fock-space basis suited to the physical situation should be more appropriate and it has been shown that at least for DHF calculations a basis of Hartree-Fock quasiparticles for constructing the projection operators satisfies a variationally determined optimum criterion.[8] An obvious generalization of this result for a correlated wave function would suggest the use of natural one-particle wave functions, i.e., the eigenfunctions of the one-particle density matrix that correspond to postive energies. This could be accomplished by a procedure that uses approximate projectors, whereby the process of obtaining new projectors from diagonalizing the one-particle density matrix and constructing a new density matrix from a correlated wave function should be iterated until self-consistency is attained. At the present time, however, such a procedure is far too complicated and a simpler method should be sought for.

In this paper we report practical calculations with a no-pair formalism employing projection operators corresponding to a particle in the external field of the nucleus. These projectors correspond more closely to the physical situation in a multielectron atom than the free-particle projectors employed earlier, especially for the inner shells, where most of the relativistic corrections originate. This approach has been pioneered by Sucher[9] and later by Douglas and Kroll,[10] who also provided an unitary transformation analogous to the Foldy-Wouthuysen (FW) transformation. The Douglas-Kroll transformation enables the decoupling of electron and positron degrees of freedom to a specified order in the coupling constant of the potential without introducing the singular operators of the FW transformation.

We continue with a short review of the method and a discussion of its application to one-electron atoms. Section IV reports on calculations of the total energy and spin-orbit splitting of the ground state ${}^2P_u$ of the bromine atom and total energy, ionization potential, and electron affinity of the silver atom. A summary of the results concludes the paper.

II. THEORY

Starting from the QED Hamiltonian in Coulomb gauge, a configuration-space Hamiltonian operating on four-component spinors can be derived,[2,3] if a one-particle basis of Fock space is specified, thus defining what an electron and a positron is like, and if the total Fock-space Hamiltonian is partitioned into a part H_0 describing a stationary n-electron state Φ_0 and a residual part describing pair creation processes. This residual part is neglected in the present context and it will be assumed that it is tractable by perturbation theory, if required. The questions of the gauge employed and the renormalization of the resulting perturbation series are discussed in Refs. 9 and 2, respectively, and are of crucial importance for the evaluation of the residual interaction. Since, however, only the no-pair part H_0 will be treated in the present context, we do not comment on these questions further.

The configuration-space Hamiltonian obtained from the no-pair part H_0 is an n-particle Dirac equation that contains the potential bracketed by projection operators on the positive energy part of the aforementioned one-particle Fock-space basis set. If a free-particle Fock-space basis set is used, the Hamiltonian can be transformed by a free-particle Foldy-Wouthuysen transformation to a representation in which upper and lower components are decoupled. The positive energy part of this operator reads

$$h_+ = \sum_i E_i + \sum_i V_{\text{eff}}(i) + \sum_{i<j} V_{\text{eff}}(i,j) , \tag{2.1}$$

with

$$E_i \equiv E_{p_i} = (p_i^2 + m^2)^{1/2} , \tag{2.2}$$

$$\begin{aligned} V_{\text{eff}} = -eA_i[&V_{\text{ext}}(i) + R_i V_{\text{ext}}(i) R_i \\ &- R_i \boldsymbol{\sigma}_i \cdot \mathbf{A}_{\text{ext}}(i) - \boldsymbol{\sigma}_i \cdot \mathbf{A}_{\text{ext}}(i) R_i] A_i , \end{aligned} \tag{2.3}$$

$$A_i = \left[\frac{m+E_i}{2E_i} \right]^{1/2} , \tag{2.4}$$

$$R_i = \frac{\boldsymbol{\sigma}_i \cdot \mathbf{p}_i}{m+E_i} , \tag{2.5}$$

$$\begin{aligned} V_{\text{eff}}(i,j) = A_i A_j \Bigg[&\frac{e^2}{|\mathbf{r}_{ij}|} + R_i \frac{e^2}{|\mathbf{r}_{ij}|} R_i + R_j \frac{e^2}{|\mathbf{r}_{ij}|} R_j \\ &+ R_i R_j \frac{e^2}{|\mathbf{r}_{ij}|} R_i R_j \Bigg] A_i A_j . \end{aligned} \tag{2.6}$$

Douglas and Kroll[10] noted that for a two-component reduction of a no-pair equation with external field projectors a generalization if the FW transformation is required. A FW transformation in an external field yields highly singular operators that cannot be easily used in practical calculations. They proposed the ansatz

$$U_1 = (1 + W_1^2)^{1/2} + W_1 \tag{2.7}$$

which furnishes a unitary operator if W_1 is an anti-Hermitian operator for a subsequent transformation:

$$\begin{aligned} U_1(\beta E_p + \mathscr{E}_1 + \mathscr{O}_1) U_1^{-1} = \beta E_p - [\beta E_i, W_1] + \mathscr{O}_1 + \mathscr{E}_1 \\ + \mathscr{O}_2 + \mathscr{E}_2 + \cdots , \end{aligned} \tag{2.8}$$

where $\mathscr{E}_1$ denotes the even part (that is, terms containing no $\boldsymbol{\alpha}$ matrices) and $\mathscr{O}_1$ the odd part (containing the $\boldsymbol{\alpha}$ matrices that couple upper and lower components) of the one particle no-pair Hamiltonian with free-particle projection operators and $\mathscr{E}_2$ and $\mathscr{O}_2$ denote even and odd parts of higher order. $\mathscr{O}_1$ is removed by imposing the condition

$$[\beta E_p, W_1] = \mathscr{O}_1 , \tag{2.9}$$

which in turn is solved for W_1, yielding an integral operator with kernel

$$\begin{aligned} W_1(\mathbf{p},\mathbf{p}') = - \Bigg[&- \frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{[2E_p(E_p+m)]^{1/2}} \left[\frac{E_{p'}+m}{2E_{p'}} \right]^{1/2} \\ &+ \frac{\boldsymbol{\alpha}\cdot\mathbf{p}'}{[2E_{p'}(E_{p'}+m)]^{1/2}} \left[\frac{E_p+m}{2E_p} \right]^{1/2} \Bigg] \\ &\times V_{\text{ext}}(\mathbf{p},\mathbf{p}') , \end{aligned} \tag{2.10}$$

$V_{\text{ext}}(\mathbf{p},\mathbf{p}')$ denoting the Fourier transform of the external potential. This operator is used in an expansion of $U_1 = (1+W_1^2)^{1/2} + W_1$ to second order in the external potential. Douglas and Kroll also show that to this order the projection operators may be replaced by $\beta^{(+)} = (1+\beta)/2$. Finally a two-component no-pair equation with external field projectors obtains, correct to second order in the potential. As an approximation for the calculation of multielectron systems we consider only the one-particle operators and retain the unmodified Coulomb interaction. At this stage the operator for zero external vector potential reads

$$H_+^{(2)} = \sum_i E_i + \sum_i V'_{\text{eff}}(i) + \sum_{i<j} \frac{e^2}{|\mathbf{r}_{ij}|} , \tag{2.11}$$

with

$$\begin{aligned} V'_{\text{eff}}(i) = A_i[&V_{\text{ext}}(i) + R_i V_{\text{ext}}(i) R_i] A_i \\ &+ W_1(i) E_i W_1(i) + \tfrac{1}{2} W_1^2(i) E_i + \tfrac{1}{2} E_i W_1^2(i) \end{aligned} \tag{2.12}$$

and the kernel of $W_1(i)$ given as above. A further approximation is made by neglecting all explicitly spin dependent operators[6] for the variational determination of the wave function. The spin-orbit coupling terms of (2.11) may be calculated by perturbation theory at a later stage. It should be stressed, however, that (2.11) is bounded from below and that therefore spin-orbit terms as well as the Breit interaction, if included in the two-particle potential, can be treated variationally, if the appropriate terms in the operator are retained.

We denote the spin-free operator by $\mathscr{H}_+$. It can be derived from $H_+^{(2)}$ by replacing all $\boldsymbol{\sigma}\cdot\mathbf{p}$ operators in R_i by $\mathbf{p}_i$, using the identity

$$(\sigma\cdot\mathbf{u})(\sigma\cdot\mathbf{v})=\mathbf{u}\cdot\mathbf{v}+i\sigma\cdot(\mathbf{u}\times\mathbf{v})\ , \tag{2.13}$$

valid for spin-independent operators **u** and **v**.

III. 1s STATES OF ONE-ELECTRON ATOMS

For practical calculations we employ the LCAO approximation (linear combination of atomic orbitals) and expand the one-particle wave functions in a series of Gaussian functions. The operators of the Hamiltonian are evaluated in this basis set and the resulting matrix representation may be used as a starting point for the calculation of energy levels and wave functions of multiparticle systems.[11]

In the case of the Hamiltonian $\mathscr{H}_+$ the matrix in the basis set of Gaussian functions could not be calculated analytically. To evaluate the operators of $\mathscr{H}_+$, which are generally given in a momentum space formulation, we diagonalized the matrix of E_i, which can be constructed analytically.[12,13] The functions of E_i occurring in the operator $\mathscr{H}_+$ are in turn evaluated on the diagonal, and the integral operator (2.10) is represented by its (nondiagonal) matrix in this particular basis set diagonalizing the relativistic kinetic energy. A reverse transformation of the resulting matrices completes the calculation of the matrix representation of $\mathscr{H}_+$. This approximation gives the correct result in the limit of an infinite basis set and can be represented by an effective nonunitary transformation of the external potential.[6]

The results for one-electron atoms are collected in Table I. A numerical analysis of the scaled binding energy

$$\epsilon(\gamma)=\frac{(E-m)}{\gamma^2 m}\ ,\quad \gamma=Z\alpha\ , \tag{3.1}$$

gives a value of -0.125 for c_2 in a power series-expansion

$$\epsilon^{\mathrm{num}}(\gamma)=-\tfrac{1}{2}+c_2\gamma^2+c_3\gamma^3+c_4\gamma^4+\cdots\ . \tag{3.2}$$

The numerical value of c_3 could be determined by extrapolating

$$c_3^{\mathrm{num}}(\gamma)=\frac{c_2^{\mathrm{num}}(\gamma)-c_2^{\mathrm{num}}(0)}{\gamma} \tag{3.3}$$

to zero. We find that c_3 vanishes to three significant figures, that is within the accuracy of the extrapolation procedure. The first term deviating from the Dirac equation result

$$\epsilon_D(\gamma)=-\tfrac{1}{2}-\tfrac{1}{8}\gamma^2-\tfrac{1}{16}\gamma^4+\cdots \tag{3.4}$$

is c_4^{num}. For this term the numerical analysis revealed a value of -0.0172 instead of -0.0625. It can thus be concluded that the one-particle energies calculated with $\mathscr{H}_+$ are in agreement with the Dirac equation results to order $(Z\alpha)^3$, and we expect the eigenvalues slightly above those of the Dirac equation.

It should be noted that the above analysis does not preclude the possibility that for $\mathscr{H}_+$ the binding energy is not an analytic function at all. Since the decoupling of the upper and lower components has only been accomplished to second order in the potential, a term proportional to $\ln\gamma$ might occur in some higher order, as is the case for the no-pair equation with free-particle projectors.[4] The ansatz (3.2) and the numerical findings can only be used to conjecture that no terms of order $(Z\alpha)^3$, i.e., larger than the leading order of the radiative corrections, are present.

IV. MANY-ELECTRON ATOMS

The operator $\mathscr{H}_+$ has been tested in *ab initio* calculation of the bromine and silver atom. A standard Roothaan-type self-consistent field (SCF) procedure was used to calculate molecular orbitals which are subsequently employed in a multireference double-excitation configuration interaction (MRD-CI) calculation.[14,15] The relativistic calculations were done with the operator $\mathscr{H}_+$, i.e., the spin-free part of the operator given in Eq. (2.11). Note that $\mathscr{H}_+$ is identical with $H_+^{(2)}$ for the 1s states of one-electron atoms. The spin-orbit splittings have been evaluated in first order of perturbation theory with the microscopic Breit-Pauli spin-orbit Hamiltonian[16] because the spin-orbit part of (2.12) was not yet implemented in the programs.

For the bromine atom, three different basis sets have been used, all derived from a basis set given by Dunning.[17] The first one is a contracted basis set of 47 functions, the details of which are given elsewhere.[18] Since the matrix method described above makes implicit use of the resolution of the identity, it seemed advisable to test the influence of the basis set size on the results. So all functions of the above basis set except for the innermost function of d symmetry were uncontracted, the latter comprising four six-component primitives in the basis set of totally 64 Gaussians. Finally, a basis set of 76 functions obtained by

TABLE I. 1s energies for one electron atoms calculated in a basis of Gaussian orbitals (in a.u./Z^2). (A basis set of 62 Gaussian functions with exponents $\zeta_i=Z^2\zeta_i'$, $\zeta_i'=8[-8]$, $1[-7]$, $2[-7]$, $4[-7]$,. . .$4[7]$, $8[7]$, $1[8]$ has been used, the numbers in brackets denoting powers of 10. The nonrelativistic energy for this basis set is $-0.499\,999\,959\,5$ a.u./Z^2.)

Z	$Z\alpha$	$\mathscr{H}_+$	Dirac equation	Z	$Z\alpha$	$\mathscr{H}_+$	Dirac equation
1	0.007 297	−0.500 006 63	−0.500 006 66	69	0.503 517	−0.535 672 84	−0.536 484 97
5	0.036 487	−0.500 166 44	−0.500 166 52	80	0.583 788	−0.550 519 41	−0.551 905 01
8	0.058 379	−0.500 426 39	−0.500 426 74	90	0.656 762	−0.567 933 96	−0.570 093 52
14	0.102 163	−0.501 308 82	−0.501 311 51	100	0.729 735	−0.590 618 90	−0.593 919 52
27	0.197 029	−0.504 919 41	−0.504 949 07	110	0.802 709	−0.621 359 44	−0.626 420 72
55	0.401 354	−0.521 576 15	−0.521 941 69	120	0.875 682	−0.666 246 40	−0.674 359 91

TABLE II. Bromine atom total energies and spin-orbit coupling for the ground state ^2P_u. The DHF value for the total energy is −2603.59 a.u. (Ref. 7), the HF limit is −2572.44 a.u. (Ref. 23), the experimental spin-orbit splitting is −3685 cm^{-1}.

Number of basis-set functions	Total energy[a] (a.u.) Nonrelativistic	$\mathscr{H}_+$	Spin-orbit splitting[b] (cm^{-1}) Nonrelativistic	$\mathscr{H}_+$
47	−2572.05	−2607.07	3187	3412
64	−2572.36	−2604.39	3222	3533
76	−2572.37	−2604.29	3182	3496

[a] SCF result.

[b] Obtained in first order of perturbation theory from a MRD-CI wave function.

TABLE III. Bromine atom orbital energies. The DHF values for p and d species have been averaged over spin-orbit components. All values given in atomic units.

	Nonrelativistic			$\mathscr{H}_+$			
	47 func	64 func	76 func	47 func	64 func	76 func	DHF
1s	−490.11	−490.06	−490.07	−499.41	−498.12	−498.14	−498.52
2s	−65.081	−65.199	−65.212	−67.086	−67.066	−67.088	−67.125
3s	−9.8467	−9.8702	−9.8784	−10.173	−10.181	−10.196	−10.200
4s	−0.9917	−0.9935	−0.9953	−1.0202	−1.0205	−1.0230	−1.0210
2p	−58.574	−58.553	−58.566	−59.021	−58.973	−58.995	−59.021
3p	−7.4744	−7.4736	−7.4812	−7.5314	−7.5318	−7.5463	−7.5509
4p	−0.4437	−0.4434	−0.4445	−0.4418	−0.4419	−0.4433	−0.4562
3d	−3.2239	−3.2188	−3.2262	−3.1437	−3.1619	−3.1641	−3.1541

TABLE IV. Expectation values of r^2 for the bromine atom. The DHF values for p and d species have been averaged over the spin-orbit components. All values are given in atomic units.

	Nonrelativistic			$\mathscr{H}_+$			
	47 func	64 func	76 fun	47 func	64 func	76 fun	DHF
1s	0.2554(−2)	0.2554(−2)	0.2554(−2)	0.2414(−2)	0.2423(−2)	0.2423(−2)	0.2459(−2)
2s	0.4422(−1)	0.4391(−1)	0.4391(−1)	0.4216(−1)	0.4204(−1)	0.4204(−1)	0.4205(−1)
3s	0.3592	0.3587	0.3584	0.3457	0.3459	0.3456	0.3453
4s	0.3485(+1)	0.3473(+1)	0.3463(+1)	0.3368(+1)	0.3364(+1)	0.3352(+1)	0.3353(+1)
2p	0.3302(−1)	0.3413(−1)	0.3413(−1)	0.3343(−1)	0.3345(−1)	0.3345(−1)	0.3348(−1)
3p	0.3744	0.3743	0.3741	0.3690	0.3689	0.3686	0.3694
4p	0.5318(+1)	0.5319(+1)	0.5304(+1)	0.5294(+1)	0.5294(+1)	0.5274(+1)	0.5192(+1)
3d	0.4162	0.4163	0.4214	0.4162	0.4172	0.4244	0.4235

TABLE V. Silver atom total energies in atomic units.[a]

Basis set number	Number of contractions[b]	Contraction[c]	Reference	Nonrelativistic	$\mathscr{H}_+$
1	13,8,4	$d3$	24	−5192.99	−5305.45
2	16,10,5	$d3$	24	−5194.32	−5306.52
3	15,10,5	$d4$	20	−5196.96	−5311.60
4	15,10,6	$d3$	20	−5196.99	−5311.29
5	17,11,6	$d3$	20	−5197.59	−5311.95 5311.62[d]
6	17,8,6	$p4d3$	25	−5197.57	−5314.97
7	17,8,8	$p4$	25	−5197.57	−5314.67
8	17,11,8		25	−5197.59	−5311.65

[a] The Hartree-Fock limit is −5197.70 a.u. (Ref. 23), the DHF energy is −5310.66 a.u. (Ref. 7).

[b] The number of contracted s-, p-, and six-component d functions is given.

[c] The notation dn (pn) denotes that the n highest exponents of d-symmetry (p-symmetry) have been contracted using the coefficients of the innermost atomic orbital in a nonrelativistic SCF calculation employing the uncontracted basis set.

[d] The operators have been evaluated using a diagonal representation of $p^2/2m$ instead of a diagonal representation of $(p^2+m^2)^{1/2}$, which has been employed unless indicated otherwise.

adding one more d primitive with exponent $\xi=0.33$ and uncontracting the function with lowest exponent from the innermost contraction of d symmetry.

From the total SCF energies in Table II it may be concluded that the basis-set deficiencies indeed lead to sizable deviations for the various basis sets. Although all of them yield nonrelativistic total energies reasonably close to the Hartree-Fock limit, we obtain results for $\mathscr{H}_+$ that differ as much as 3 hartrees for the smallest and the largest basis set. Especially the repulsive correction term connected with the integral operator in the second line of Eq. (2.12) seems to be quite sensitive to the fulfillment of the completeness relation. Therefore the operator is calculated systematically too small for an incomplete resolution of the identity, and we find a higher energy value for the larger basis set.

Nevertheless, all of the values yield a relativistic correction which agrees within a few percent with the corresponding quantity obtained from Dirac-Hartree-Fock (DHF) calculations. It should be borne in mind that the total energies are only of secondary importance and that the relativistic correction to the charge distribution leading to relativistic excitation energies and property values is the main point of interest in electronic structure calculations for atoms and molecules.

The properties of the charge distribution may be judged from the spin-orbit coupling values which show marked relativistic corrections in good agreement with experiment. The increase may be understood by considering the spatial contraction of the $4p$ orbital which can be inferred from comparison of the orbital energies and $\langle r^2 \rangle$ values with their nonrelativistic counterparts in Tables III and IV.

Note that the $\langle r^2 \rangle$ values cannot be compared directly with the corresponding DHF results, since like all operators they must first be transformed to the DHF four-component (Minkowski) representation by a transformation inverse to the one used to obtain the two-component (quasi-Newton) representation.[19] This process will generally introduce terms of leading relative order $(Z\alpha)^2$ which effectively limit the possibility of direct comparison of the corresponding values given in Table IV. Note also that the nonrelativistic values also deviate for the various basis sets, especially for the outer (valence) shell. This shows that large basis sets are desirable, of course, not only for the matrix representation of $\mathscr{H}_+$, but also to achieve better convergence of the nonrelativistic results.

Similar results were obtained for the SCF ground state of the silver atom, for which a larger variety of basis sets described in Table V has been tested. We also included basis sets yielding nonrelativistic energies several hartrees away from the Hartree-Fock limit, but still giving relativistic corrections within a few percent of the DHF value. For a contraction of the inner shells (basis sets 6 and 7) we again find that the replusive term in (2.12) is calculated too small, leading to an overestimation of the relativistic correction of about 4%.

We conclude that generally basis sets of this quality should be left uncontracted for the matrix representation of the integral operator in (2.12). A sufficiently converged representation seems to be attained with basis set no. 5. For this basis set a calculation has been carried out evaluating the matrix of the relativistic kinetic energy from the matrix of $p^2/2m$. The result is in reasonable agreement with the corresponding value, for which the E_i matrix has been obtained analytically.

As a more difficult test of the $\mathscr{H}_+$ operator we choose the calculation of the ionization potential and the electron affinity for the silver atom. For these calculations basis set no. 4 was chosen because it contains several semidiffuse functions which are needed for a description of the charge distribution of the negative ion. The results are collected in Tables VI and VII. These quantities may be compared with literature data, which are mostly obtained on the Hartree-Fock level.[20,21] They report values for the relativistic correction to the ionization potential ranging from 0.42 to 0.50 eV, in good agreement with the $\mathscr{H}_+$ result of 0.38 eV. The large difference of about 1.2 eV to the experimental value is attributed to the correlation contribution, which in part could be recovered by the CI treatment. Employing a reference space of one configuration, we find 0.33 eV of correlation contribution in the nonrelativistic and 0.42 eV in the relativistic case. This indicates that correlation effect and relativistic contribution to the ionization potential are nonadditive.

A substantial improvement of the basis set by including f-type functions could only be accomplished on the nonrelativistic level, since the required operators for $\mathscr{H}_+$ were implemented only up to d functions. The inclusion of an f function with exponent $\zeta=1.2$ improved the ionization potential by as much as 0.24 eV, but the optimization of the exponent finally yielded an improvement of only 0.13 eV. Adding this correction to the relativistic d-function result, we obtain our best value of 6.85 eV. These findings show that the basis set is far from converged even for the nonrelativistic calculation of the correlation contribution and that a proper treatment should include functions of

TABLE VI. Ionization potential of the silver atom (in eV). Basis set no. 4 has been used unless indicated otherwise.

Koopmans's theorem, nonrelativistic	5.97
Koopmans's theorem, $\mathscr{H}_+$	6.38
Difference of nonrelativistic Hartree-Fock energies (Ref. 20)	5.91
$\mathscr{H}_+$, difference of SCF energies	6.29
Dirac-Hartree-Fock[a] (Ref. 21)	6.34
Cowan-Griffin operator[b] (Ref. 20)	6.33
Cowan-Griffin operator[c] (Ref. 20)	6.41
Relativistic effective core potential (Ref. 21)	6.34
Nonrelativistic CI	6.24
Same, one f-function with $\zeta=1.2$	6.48
Same, one f-function with $\zeta=1.7$[d]	6.38
$\mathscr{H}_+$, CI	6.71
Experiment (Ref. 26)	7.57

[a] Obtained with Desclaux's program.

[b] Cowan-Griffin operator (Ref. 27) employed in Hartree-Fock calculation.

[c] Cowan-Griffin operator in first order of perturbation theory.

[d] Optimized value, minimizing the nonrelativistic CI energy of the neutral species.

TABLE VII. Electron affinity of the silver atom (in eV). Basis set no. 4 has been used unless indicated otherwise.

Difference of Hartree-Fock energies (Ref. 22)	−0.04
$\mathscr{H}_+$, Difference of SCF energies	−0.08
Cowan-Griffin operator[a] (Ref. 20)	−0.16
Relativistic effective core potential, CI (Ref. 21)	0.71
Nonrelativistic CI	0.85
Same, one f-function with $\zeta = 1.2$	0.90
Same, one f-function with $\zeta = 1.7$[b]	0.90
$\mathscr{H}_+$, CI	1.00
Experiment (Ref. 28)	1.30

[a] Cowan-Griffin-operator (Ref. 27) in first order of perturbation theory.

[b] Optimized value, minimizing the nonrelativistic CI energy of the neutral species.

still higher angular momentum, as has already been noted by other authors in the study of transition metal atoms.[22]

For the electron affinity much better agreement with experiment was obtained. In this case the Hartree-Fock calculation gives disastrous results, even of the incorrect sign. On CI level the relativistic correction was calculated to be 0.14 eV, yielding a relativistic electron affinity of 0.98 eV with the basis set comprising only d functions. If we add the effect of the optimized f function to this number, we get 1.05 eV in reasonable agreement with the experimental 1.30 eV.

V. SUMMARY

Devising an approximate scheme for the calculation of atomic and molecular structure by means of a relativistic two-component formalism the no-pair-Hamiltonian with external field projectors as transformed by a Douglas-Kroll transformation presents the following advantages.

(1) It can be derived from quantum electrodynamics;

(2) the binding energies for one-electron atoms agree to order $(Z\alpha)^3$ with those of the Dirac equation;

(3) it approaches the correct nonrelativistic limit, may be treated variationally, and avoids the shortcomings of molecular four-component methods based on basis set expansion techniques;

(4) it may be used in connection with standard programs for electronic structure calculation, whereby the computational effort for implementing the relativistic corrections is negligible for a calculation of the type as reported in the present paper.

The most important shortcoming of the present method of evaluating the integrals is the demand for large basis sets in order to ensure a good matrix representation. Much progress has been made, however, in the analytical evaluation of the operators of the free-particle projectors even for the molecular case,[12] which should be of great value also for the evaluation of the operators of $\mathscr{H}_+$.

A further refinement of the theory by including still higher orders of $Z\alpha$, although in principle possible by iteration of the Douglas-Kroll transformation, does not seem to be advisable, since the radiative corrections are larger than the largest term that could be recovered in addition to $\mathscr{H}_+$. On the other hand, the (possibly analytical) evaluation and variational treatment of the correct spin-orbit operators and the investigation of the relation of relativistic and correlation effects as well as a study on the effect of the pair-creation part, which has been neglected so far entirely, could open very interesting perspectives for future research.

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