

Applicability of the no-pair equation with free-particle projection operators to atomic and molecular structure calculations

Bernd A. Hess

*Bergische Universität, Gesamthochschule Wuppertal, Fachbereich 9, Theoretische Chemie,
Gauss-Strasse 20, 5600 Wuppertal 1, West Germany*

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The no-pair equation with free-particle projection operators proposed by Sucher is employed for linear combination of atomic orbital calculations on one-electron atoms and a self-consistent-field configuration-interaction calculation of the ground-state energy and the spin-orbit splitting of the bromine atom. A matrix technique used for the representation of the required operators is discussed. Comparison of the results with Dirac-Hartree-Fock calculations shows that no-pair Hamiltonians furnish a convenient approximation for introducing relativistic effects in atomic and molecular structure calculations.

I. INTRODUCTION

In a recent paper by Hardekopf and Sucher¹ the numerical properties of the no-pair equation with free-particle projection operators² are discussed. The authors find that the eigenvalues of the corresponding Hamiltonian h_+ can be used as an approximation to the energy of multiparticle bound states in a way that is consistent with quantum electrodynamics (QED). The residual interaction, that is the difference between the exact QED Hamiltonian H and the no-pair Hamiltonian with free-particle projectors h_+ , must be treated by perturbation theory.¹⁻³ The question of renormalization of the perturbation series, is, however, unsolved as yet, so the actual calculation of the higher-order terms is not easily feasible to date. In the present paper we will neglect the residual interaction altogether and rather employ h_+ in a *variational* treatment of ground and excited states of atomic and molecular systems in a way that permits the systematic inclusion of correlation effects into the calculation, thus going beyond the Hartree-Fock or Dirac-Hartree-Fock (DHF) level. The operators of the Breit-Pauli Hamiltonian cannot be used for this purpose, since mass-correction operators as well as spin-orbit operators lead to a variational collapse due to their unboundedness below.

Methods that are derived from a non-Hamiltonian approach⁴ avoid the renormalization problems mentioned above, but have eventually to cope with the problems of four-component molecular DHF calculations, which have been summarized recently.⁵

From a pragmatic point of view the use of the Hamiltonian h_+ appears to be attractive for atomic and molecular structure calculations since it operates on two-component spinors, thus saving a great deal of the computational effort required for four-component molecular calculations. Moreover, the highly developed methods for describing correlation in nonrelativistic many-particle systems can be used with only minor modifications for the relativistic case. In this paper the MRD-CI (multi-reference double-excitation configuration-interaction) method^{6,7} will be employed for a calculation of the

ground-state spin-orbit splitting of the bromine atom. This method has been proven to give very reliable results not only for the calculation of energy levels for ground and excited states of molecules in the framework of the nonrelativistic Schrödinger equation,⁸ but also employing operators derived from the Breit-Pauli Hamiltonian for the calculation of fine-structure effects⁹ by perturbation theory. In fact, the aforementioned motivation for the use of two-component spinors in the relativistic case led to the development of a two-component representation of the kinetic energy operator for relativistic calculations¹⁰ which coincides with the effective kinetic energy part of the no-pair Hamiltonian h_+ . This representation of the kinetic energy has been used in a study of the ground and the first excited state of the bromine atom¹¹ and for the ground state of the CBr molecule.¹²

In the present paper, the methods employed in Ref. 10 are used to obtain a matrix representation of Sucher's no-pair Hamiltonian with free-particle projection operators. After a short review of the no-pair equations, the approximation of h_+ in the framework of an LCAO expansion (linear combination of atomic orbitals) is introduced and applied to energy levels of one-electron atoms. The results are compared with those from numerical integration techniques used in Ref. 1. Subsequently, the relativistic corrections to the one-electron operators are used to calculate the ground-state energy and spin-orbit splitting of the bromine atom. A comparison with previous results¹¹ and DHF calculations¹³ shows that no-pair Hamiltonians give promising results also for many-electron systems. A discussion of the implementation of the two-electron operators and the properties of h_+ relevant for molecular structure calculations concludes the paper.

II. NO-PAIR HAMILTONIANS IN CONFIGURATION SPACE

In this section the origin of the no-pair equations from QED is briefly reviewed. The details of the derivation may be found in Refs. 2 and 3. The formulation of Hamiltonians for the bound-state problem is accomplished by starting with the QED Hamiltonian H in Coulomb gauge

$$\begin{aligned}
H = & \int d^3x: \psi^\dagger(\mathbf{x})[-i\boldsymbol{\alpha}\cdot\mathbf{D} + \beta m + V_{\text{ext}}(\mathbf{x})]\psi(\mathbf{x}): \\
& + \frac{1}{2} \int d^3x:(\mathbf{E}_t^2 + \mathbf{B}^2): \\
& + e^2 \int \int d^3x d^3x' \frac{1}{|\mathbf{x} - \mathbf{x}'|} \\
& \times : \psi^\dagger(\mathbf{x})\psi(\mathbf{x}): : \psi^\dagger(\mathbf{x}')\psi(\mathbf{x}'):, \quad (2.1)
\end{aligned}$$

where $\psi(\mathbf{x})$ is the spinor field, \mathbf{E}_t is the transverse electric and \mathbf{B} the magnetic field, $\mathbf{D} = \partial - ie\mathbf{A}_{\text{ext}}(\mathbf{x})$, $\mathbf{A}_{\text{ext}}(\mathbf{x})$ the external vector potential, with the colons indicating normal ordering. A fixed reference time $t=0$ has been chosen.

The terms in (2.1) can be identified as

(i) the energy operator for the matter field interacting with external potential,

(ii) the energy of the transverse radiation field,

(iii) the Coulomb interaction of the matter field.

The idea is first to split off from H a part H_0 that can be used in a multiparticle Dirac equation

$$(H_0 - E_0)|\Phi_0\rangle = 0 \quad (2.2)$$

with $|\Phi_0\rangle$ describing a stationary state

$$\begin{aligned}
|\Phi_0\rangle = & \int d^3x_1 \cdots \int d^3x_N u(\mathbf{x}_1 \cdots \mathbf{x}_N) \psi^\dagger(\mathbf{x}_1) \cdots \\
& \times \psi^\dagger(\mathbf{x}_N) |0\rangle, \quad (2.3)
\end{aligned}$$

where $\psi^\dagger(\mathbf{x}_i)$ denotes a suitably chosen electron creation operator for the i th one of the N particles and $|0\rangle$ the vacuum state, and spin indices have been suppressed. The residual interaction $H_{\text{int}} = H - H_0$ will be neglected in the present context.

The ansatz of $|\Phi_0\rangle$ as product of electron creation operators only leads to an N -particle Dirac equation where the relevant operators are bracketed by positive energy projection operators, the detailed structure of which depends on the specific expansion of the matter field in terms of electron and positron operators

$$\psi(\mathbf{x}) = \sum_n U(n)u_n(\mathbf{x}) + \sum_n V^\dagger(n)v_n(\mathbf{x}), \quad (2.4)$$

where $U^\dagger(n)$ creates an electron and $V^\dagger(n)$ a positron and the wave functions $u_n(\mathbf{x})$ and $v_n(\mathbf{x})$ may be considered in the general case as arbitrary expansion coefficients. H_0 is now constructed in a way such that terms that describe the creation and destruction of virtual pairs as well as the energy of the transverse radiation field are left in the interaction part H_{int} , therefore the term "no-pair Hamiltonian" has been adopted for H_0 .² In this paper we restrict ourselves to the case where $u_n(\mathbf{x})$ and $v_n(\mathbf{x})$ denote plane-wave eigenfunctions of the free-particle Dirac Hamiltonian. The projection operators occurring in H_0 are then given by

$$\Lambda_+(\mathbf{x}) = \frac{(-\Delta + m^2)^{1/2} + (-i\partial + \beta m)}{2(-\Delta + m^2)^{1/2}} \quad (2.5)$$

which reduces to an algebraic operator in momentum space. Other choices may be more appropriate^{2,14} but lead to still more complicated operators that are nonlocal even in momentum space.

The resulting H_0 can now be subjected to a (pseudo) unitary Foldy-Wouthuysen transformation

$$W(\mathbf{p}) = \left[\frac{2E_p}{E_p + m} \right]^{1/2} \Lambda_+(\mathbf{p}) \frac{1 + \beta}{2}, \quad (2.6)$$

$$E_p = (p^2 + m^2)^{1/2}, \quad (2.7)$$

$$\Lambda_+(\mathbf{p}) = \frac{E_p + \boldsymbol{\alpha}\cdot\mathbf{p} + \beta m}{2E_p}, \quad (2.8)$$

thus transforming the four-spinor wave function $u(\mathbf{x}_1 \cdots \mathbf{x}_N)$ of (2.3) to a set of two-spinor wave functions such that in momentum space the spinors are given by

$$u(\mathbf{p}_i) = W(\mathbf{p}_i)\chi. \quad (2.9)$$

Here χ denotes a constant spinor.

In this way one obtains various no-pair equations with free particle projectors that operate on two-component spinors, the detailed structure of the resulting Schrödinger-Pauli Hamiltonians still depending on the choice of H_0 .

Three different partitions of H appear to be relevant for this paper, the first one of which is given in Ref. 2 and yields

$$h_+ = \sum_i E_i + \sum_i V^{\text{eff}}(i) + \sum_{i < j} V^{\text{eff}}(i, j) \quad (2.10)$$

with

$$E_i = (p_i^2 + m^2)^{1/2}, \quad (2.11)$$

$$\begin{aligned}
V^{\text{eff}}(i) = & -eA_i[V_{\text{ext}}(i) + R_i V_{\text{ext}}(i)R_i \\
& - R_i \boldsymbol{\sigma}_i \cdot \mathbf{A}_{\text{ext}}(i) \\
& - \boldsymbol{\sigma}_i \cdot \mathbf{A}_{\text{ext}}(i)R_i]A_i, \quad (2.12)
\end{aligned}$$

$$A_i = [(m + E_i)/2E_i]^{1/2}, \quad (2.13)$$

$$R_i = \boldsymbol{\sigma}_i \cdot \mathbf{p}_i / (m + E_i), \quad (2.14)$$

$$\begin{aligned}
V^{\text{eff}}(i, j) = & A_i A_j \left[\frac{e^2}{r_{ij}} + R_i \frac{e^2}{r_{ij}} R_j + R_i \frac{e^2}{r_{ij}} R_i \right. \\
& \left. + R_i R_j \frac{e^2}{r_{ij}} R_i R_j \right] A_i A_j. \quad (2.15)
\end{aligned}$$

It is also possible to include the Breit interaction here as the leading term of the interaction between two electrons mediated by a transverse photon.

The second no-pair Hamiltonian, which will be subsequently used for the calculation of the ground state of the bromine atom, is a modification of Eq. (4.10) in Ref. 3. The equation given there is

$$h'_+ = \sum_i E_i + \sum_i V^{\text{eff}}(i) + \sum_{i < j} e^2/r_{ij}. \quad (2.16)$$

In this equation the Coulomb interaction is retained unchanged, thus avoiding the complicated spin dependence in the two-electron operators of (2.10). The modification mentioned above encompasses the subtraction of the external-field spin-orbit interaction,

$$\sum_i h_{s.o.}(i) = \sum_i \frac{A_i}{m + E_i} i\sigma_i \cdot [\mathbf{p}_i V_{\text{ext}}(i) \times \mathbf{p}_i] \frac{A_i}{m + E_i}, \quad (2.17)$$

from V^{eff} in (2.16), thus giving an operator that differs from the nonrelativistic case in that all one-electron operators are replaced by the spin-dependent one-electron operators of the no-pair equation (2.10) or (2.16). It reads

$$h_+'' = \sum_i E_i + \sum_i V^{\text{eff}}(i) + \sum_{i < j} e^2/r_{ij} \quad (2.18)$$

with

$$V^{\text{eff}} = -e \left[A_i V_{\text{ext}}(i) A_i + \frac{A_i}{m + E_i} \mathbf{p}_i V_{\text{ext}}(i) \mathbf{p}_i \frac{A_i}{m + E_i} \right], \quad (2.19)$$

where \mathbf{A}_{ext} has been assumed to be zero and the operator relation $(\boldsymbol{\sigma} \cdot \mathbf{A} \boldsymbol{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B})$ has been used to split $R_i V_{\text{ext}}(i) R_i$ into a spin-dependent and a spin-independent part. The reason for preferring operator h_+'' to h_+' is not only its simplicity of implementation, but also the fact that including the one-electron spin-orbit operators while leaving out all two-electron spin-orbit operators is quite inconsistent with the finding that two-electron terms effectively shield the one-electron spin-orbit interaction. In fact, since the two-electron terms reduce the one-electron interaction by a factor of $\frac{1}{2}$ as a rule of thumb,¹⁵ h_+' would lead to a spin-orbit interaction which is much too large. Using the operator h_+'' , the spin-orbit coupling may be calculated at the CI level to first order in perturbation theory. In the present study this has been done using the nonrelativistic spin-orbit coupling operators,⁹ since programs employing the full two-electron part of h_+ are not yet available.

The partition

$$h_+^{\text{SQR}} = \sum_i E_i + \sum_i V_{\text{ext}}(i) + \sum_{i < j} e^2/r_{ij} \quad (2.20)$$

given in Eq. (4.12) of Ref. 3 is the simplest possible partition of H and has been used as effective kinetic energy operator in Ref. 10. It will be used in this paper to provide a test of the accuracy of the matrix representation of operators h_+ and h_+' .

The question as to which of the possible operators is a suitable choice for a given bound-state problem can only be answered by applying them in an actual calculation. This has been done for the operator (2.10) for one- and two-electron systems in a momentum-space formulation using numerical integration of the equations.¹

In order to study the applicability of h_+ in LCAO expansions as they are commonly used in atomic and molecular structure calculations, the one-electron atoms again provide a convenient starting point.

III. LCAO APPROXIMATION TO THE OPERATORS OF THE NO-PAIR HAMILTONIAN

The LCAO approximation uses a matrix representation of the relevant operators in a basis of suitably chosen one-electron functions $\{\phi_i\}$. The matrix representation is

usually constructed in coordinate space. However, since the operators in Eqs. (2.10) and (2.16) are nonlocal in coordinate space, a momentum-space representation seems appropriate.¹ Using a basis set of Gaussian orbitals, the first part of (2.10) representing the kinetic energy can be evaluated analytically in terms of modified Bessel functions.¹⁶ A different approach has been used in Ref. 10. Since the complicated integrals arising from the potential term could not be evaluated analytically, the method introduced in Ref. 10 will be used for all the operators in (2.10).

The matrix of E_i can be easily constructed in a complete basis set in which p_i^2 is diagonal. This requires, however, an infinite number of basis functions. An approximation is furnished by the assumption that the resolution of the identity also holds in the finite-dimensional case. So we diagonalize the matrix of the nonrelativistic kinetic energy $p^2/2m$, compute E_i on the diagonal, and transform the modified matrix back to the original basis.

The potential operators may be treated in the same way. The eigenvector matrix of $p^2/2m$ transforms $V_{\text{ext}}(x)$ to a basis in which p^2 is approximately diagonal, the p^2 -dependent operators are evaluated from E_i , and the resulting matrices transformed back.

This process may be represented by a simple matrix multiplication that shows that the method corresponds to a different metric for the evaluation of the matrix of V_{ext} and certain corrections to the potential. Employing standard matrix techniques, we get for the effective potential

$$\begin{aligned} \tilde{V}_\phi^{\text{eff}} &= (\tilde{S} \tilde{X} \tilde{U}) \tilde{Y} (\tilde{X} \tilde{U})^T \tilde{V}_\phi (\tilde{X} \tilde{U}) \tilde{Y} (\tilde{S} \tilde{X} \tilde{U})^T \\ &= \tilde{M} \tilde{V}_\phi \tilde{M}^T, \end{aligned} \quad (3.1)$$

where \tilde{S} is the overlap matrix of the original basis set $\{\phi_i\}$, \tilde{X} is the transformation matrix to an orthogonal basis set $\{x_i\}$ obtained by Schmidt-orthogonalization, and \tilde{U} is the unitary matrix that diagonalizes the matrix of the kinetic energy. \tilde{Y} represents the diagonal matrix of the kinematical factors in (2.10).

In this way the effect of the A_i and R_i operators in (2.10) may be represented by an effective (nonunitary) two-index transformation $\tilde{V}^{\text{eff}}(i) = \tilde{M} \tilde{V}(i) \tilde{M}^T$, where \tilde{M} is given by (3.1). For the two-electron operators a four-index transformation is required. The discussion of the most economic way to effect this transformation is deferred to Sec. V. Assuming that the external vector potential is zero, we get from (2.10)

$$V^{\text{eff}}(i) = -e A_i V_{\text{ext}}(i) A_i - e A_i R_i V_{\text{ext}}(i) R_i A_i.$$

In order to evaluate the matrix of the first term, we chose $(Y)_{ii} = A_i$ in (3.1). The second term reads

$$\frac{A_i}{m + E_i} (\boldsymbol{\sigma}_i \cdot \mathbf{p}_i) V_{\text{ext}}(i) (\boldsymbol{\sigma}_i \cdot \mathbf{p}_i) \frac{A_i}{m + E_i}. \quad (3.2)$$

If the operator identity $(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B})$ is employed, we get again two terms,

TABLE I. 1s energies for one-electron atoms calculated in a basis set of Gaussian orbitals. Energies in a.u./Z².

	Z = 1	Z = 5	Z = 8	Z = 14	Z = 27	Z = 55	Z = 69
Z α	0.007 297 35	0.036 486 76	0.058 378 82	0.102 162 94	0.197 028 52	0.401 354 39	0.503 517 32
No-pair eq., 62 orb. ^a	-0.500 002 44	-0.500 181 81	-0.500 484 85	-0.501 573 32	-0.506 370 23	-0.530 464 13	-0.552 119 33
No-pair eq., 62 orb. ^b	-0.500 006 78	-0.500 182 31	-0.500 484 91	-0.501 573 35	-0.506 370 25	-0.530 464 14	-0.552 119 32
No-pair eq., 36 orb. ^c	-0.500 002 44	-0.500 181 72	-0.500 484 69	-0.501 572 95	-0.506 369 05	-0.530 453 83	-0.552 085 66
SQR, ^d 62 orb.	-0.500 028 63	-0.500 798 32	-0.502 007 41	-0.505 983 37	-0.521 765 38	-0.600 673 78	-0.687 731 75
SQR, ^e 62 orb.	-0.500 032 94	-0.500 798 80	-0.502 007 50	-0.505 983 37	-0.521 765 37	-0.600 673 74	-0.687 731 73
Dirac equation	-0.500 006 66	-0.500 166 52	-0.500 426 74	-0.501 311 51	-0.504 949 07	-0.521 941 69	-0.536 484 97
Experiment ^f	-0.500 005 5 ^g	-0.500 139 8 ^h	-0.500 357 4 ⁱ				

^aA basis set of 62 Gaussian functions with exponents $\xi_i = Z^2 \xi'_i$, $\xi'_i = 8(-8), 1(-7), 2(-7), 4(-7), 8(-7), 1(8)$, has been used, the numbers in parentheses denoting powers of 10; the value of the nonrelativistic energy which is $-0.499\,999\,959\,5$ a.u./Z² compared with the exact value of 0.5 a.u./Z² may be used to estimate the error introduced by the LCAO approximation in the given basis set.

^bValues obtained from a diagonalized matrix of the analytically calculated E_p .

^cBasis set of 36 Gaussian functions, $\xi'_i = 2(-5), 4(-5), \dots, 8(3), 1(4)$; the nonrelativistic energy is $-0.499\,999\,559$.

^dThe operator SQR is a matrix representation of h_+^{SOR} .

^eThe matrix of operator h_+^{SOR} has been evaluated analytically in the given basis.

^fThe values are taken from Ref. 17 and corrected for nuclear kinetic energy.

^gNuclear kinetic energy correction is $0.000\,272\,2$ a.u./Z².

^hNuclear kinetic energy correction is $0.000\,024\,76$ a.u./Z².

ⁱNuclear kinetic energy correction is $0.000\,017\,03$ a.u./Z².

TABLE II. Energies for 2s and 2p states of one-electron atoms in a basis of Gaussian orbitals. The three entries correspond to the $2s_{1/2}$, $2p_{1/2}$, and $2p_{3/2}$ states, respectively. Energies are given in a.u.

	Z = 1	Z = 5	Z = 8	Z = 14	Z = 27	Z = 55	Z = 69
No-pair eq., 36 fns. ^a	-0.125 001 07	-3.126 342 5	-8.008 977 0	-24.586 641	-92.379 701	-402.114 27	-659.103 76
	-0.125 001 57	-3.226 289 6	-8.008 514 1	-24.580 171	-92.245 404	-398.367 16	-647.295 45
	-0.124 999 91	-3.125 249 1	-8.001 690 2	-24.516 001	-91.346 917	-381.926 69	-604.434 94
No-pair eq., 36 fns. ^b	-0.125 001 07	-3.126 342 5	-8.008 977 0	-24.586 641	-92.379 701	-402.114 27	-659.103 76
	-0.125 001 58	-3.126 290 2	-8.008 524 2	-24.580 455	-92.259 743	-399.496 52	-652.281 48
	-0.124 999 91	-3.125 249 2	-8.001 692 7	-24.516 071	-91.350 298	-382.150 70	-605.343 96
Dirac equation	-0.125 002 08	-3.126 301 0	-8.008 535 5	-24.580 351	-92.253 571	-398.956 30	-649.793 41
	-0.125 002 08	-3.126 301 0	-8.008 535 5	-24.580 351	-92.253 571	-398.956 30	-649.793 41
	-0.125 000 42	-3.125 260 1	-8.001 704 8	-24.516 003	-91.347 173	-382.010 54	-604.866 36
Experiment ^c	-0.125 002 0 ^d	-3.126 216 ^e	-8.007 972 ^f				
	-0.125 002 2	-3.126 298	-8.008 519				
	-0.125 000 5	-3.125 258	-8.001 703				

^aSpin-orbit coupling in first-order perturbation theory.

^bSpin-orbit coupling included in variational procedure.

^cTaken from Ref. 17 and corrected for nuclear kinetic energy.

^dNuclear kinetic energy correction is $0.000\,068\,1$ a.u.

^eNuclear kinetic energy correction is $0.000\,155$ a.u.

^fNuclear kinetic energy correction is $0.000\,272$ a.u.

$$\frac{A_i}{m+E_i} \mathbf{p}_i V_{\text{ext}}(i) \mathbf{p}_i \frac{A_i}{m+E_i} + \frac{A_i}{m+E_i} i\boldsymbol{\sigma} \cdot [\mathbf{p}_i V_{\text{ext}}(i) \times \mathbf{p}_i] \frac{A_i}{m+E_i} \quad (3.3)$$

The first one describes an attractive spin-independent relativistic correction to the potential similar to the Darwin term and may be evaluated by (3.1) using $(Y)_{ii} = A_i/(m+E_i)$ to transform the matrix

$$V'_{kl} = \int \phi_k(-i\nabla) V_{\text{ext}}(-i\nabla) \phi_l d^3x$$

which can be easily computed in a basis of Gaussian functions. The second term is the usual external-field spin-orbit coupling operator multiplied by $2m^2c^2$ and the right order of magnitude reestablished by the kinematical factors $A_i/(m+E_i)$, which also introduce a cutoff for high momentum, so that the spin-orbit operator no longer possesses the strong singularity for $r_i \rightarrow 0$. In fact, if we look at the scaling properties of $\int e^{-\xi r^2} h_{s.o.} e^{-\xi r^2} d^3x$, with respect to ξ , we find that the spin-orbit coupling for $p \rightarrow \infty$ is proportional to ξ for the operator extracted from h_+ (similar to the other terms of the potential). The nonrelativistic spin-orbit coupling, on the contrary, scales as ξ^3 and leads soon to a variational collapse if it is included into a variational procedure employing basis functions with very high exponents. The relativistic spin-orbit coupling may be included in the variational procedure without causing trouble. The evaluation is straightforward from (3.1).

IV. THE LOW-LYING STATES OF ONE-ELECTRON ATOMS

As discussed in Ref. 1 the eigenvalues of (2.10) for the $1s$ state of a hydrogenic atom depend on $\gamma = Z\alpha$ by

$$\epsilon(\gamma) = -\frac{1}{2} - \frac{1}{8}\gamma^2 + c_3\gamma^3 + O(\gamma^4 \ln \gamma), \quad (4.1)$$

where $\epsilon(\gamma)$ denotes the scaled energy $(E-m)/\gamma^2 m$, E being the total relativistic energy. The coefficient c_3 is given by

$$c_3\gamma^5 m = \frac{4\gamma^2}{3m} |\langle \phi_{n0} | \delta(\gamma) | \phi_{n0} \rangle|^2. \quad (4.2)$$

The expectation value is to be taken over the nonrelativistic wave functions ϕ_{n0} . For $1s$ states, $c_3 = -4/3\pi \approx -0.42441$.

For the Dirac equation, on the contrary, the dependence of the eigenvalues on γ is given by

$$\epsilon_D(\gamma) = -\frac{1}{2} - \frac{1}{8}\gamma^2 - \frac{1}{16}\gamma^4 + \dots \quad (4.3)$$

Comparison of (4.1) with (4.3) shows that the energy levels of h_+ are always below the levels of the Dirac equation and differ from those by a term of order γ^3 . This is the effect of the projection operators present in the Dirac equation (2.2) introduced with the specific choice of the Fock space basis (2.4). The corrections to (2.10) can be looked upon as modified "radiative corrections" in a way similar to the treatment of the more subtle effects not included in the Dirac equation.

The methods described in Sec. III have been applied in LCAO calculations with two different basis sets of Gaussian s functions. The exponents of the basis sets and the energy values for various hydrogenic atoms are given in Table I. The row labeled *SQR* refers to calculations with the operator h_+^{SQR} in the matrix representation as described in Sec. III, and *SQRA* refers to a calculation for which all matrix elements of h_+^{SQR} have been evaluated analytically. They are included here to provide an estimate of the accuracy of the matrix method introduced in Sec. 3.

Comparison of the two values shows differences of 1 part in 10^5 for $Z=1$ to $Z=3$, which turned out to be too inaccurate to extract the coefficients of expansion (4.1) from the numerical results by extrapolation to $\gamma=0$. Starting from $Z=5$, however, the accuracy increases. The results for $Z=1-3$ are better if a diagonal representation of E_p is used instead of a diagonal representation of $p^2/2m$, that is if $(p^2+m^2)^{1/2}$ is evaluated directly in the given basis of Gaussian functions¹⁶ and diagonalized in order to calculate the E_p -dependent operators in h_+ . They are also given in the fourth row of Table I. The values for larger Z are not altered significantly by this procedure. The results for $Z=5, 8$, and 14 have been used to extrapolate the functions

TABLE III. Energies obtained with small basis sets. Energies in a.u.

Atom	Basis set ^a	No-pair eq.	Nonrel.	<i>SQR</i>	<i>SQRA</i>	No-pair eq. ^b
Br $1s$	11/16	-625.099 26	-612.495 49	-625.471 20	-654.518 07	-626.166 07
Br $1s$	16/16	-626.100 34	-612.495 53	-657.404 54	-657.424 22	-626.166 07
I $1s$	20/20	-1482.561 3	-1404.486 4	-1658.531 5	-1658.798 4	-1483.120 0
Br $2p$	8/12	-153.957 58	-152.575 62	-153.871 65	-153.934 02	-154.607 89
Br $2p$	12/12	-154.603 44	-153.123 01	-154.583 97	-154.584 33	-154.607 89

^a n/m denotes a basis set of m primitive Gaussians contracted to n functions as given in the reference. See Ref. 11 for details of the bromine basis set. Iodine basis set is taken from Ref. 18.

^bBasis of 62 Gaussians for s states, basis of 36 Gaussians for p states.

TABLE IV. Bromine atom total and orbital energies. All energies except spin-orbit coupling values in a.u.

	Nonrelativistic ^a	DHF ^b	No-pair equation ^c
Total energy	-2572.0470	-2603.59	-2609.1141
Spin-orbit splitting (cm ⁻¹) ^d	-3187.1		-3393.5
Orbital energies			
1s	-490.11	-498.5220	-500.48
2s	-65.081	-67.1250	-67.224
3s	-9.8467	-10.1996	-10.1993
4s	-0.99172	-1.0210	-1.0227
2p	-58.5741	-58.4337	-59.003
3p	-7.4744	-7.4624	-7.5306
4p	-0.44374	-0.4493	-0.4414
3d	-3.2239	-3.1370	-3.1465

^aSCF calculation; basis set and other details are given in Ref. 11. Spin-orbit coupling is calculated in first-order perturbation theory from a wave CI wave function generated from selected single and double replacements from a single reference configuration as described in Ref. 11.

^bValues taken from Ref. 13. The two entries for *p* and *d* states refer to the $p_{1/2}, p_{3/2}$ and $d_{3/2}, d_{5/2}$ states, respectively.

^cSCF calculation using h_+'' as Hamiltonian operator. Spin-orbit coupling has been evaluated as expectation value of a CI wave function similar to the treatment described in footnote b.

^dThe experimental value is -3685 cm^{-1} (Ref. 17).

$$c_2^{\text{num}}(\gamma) = [\epsilon^{\text{num}}(\gamma) - \epsilon^{\text{num}}(0)] / \gamma^2 \quad (4.4)$$

and

$$c_3^{\text{num}}(\gamma) = [c_2^{\text{num}}(\gamma) - c_2^{\text{num}}] / \gamma \quad (4.5)$$

to zero, thus providing estimates for the coefficients in (4.1). Here $\epsilon^{\text{num}}(\gamma)$ denotes the numerical $\epsilon(\gamma)$ and c_2^{num} the value for $c_2(\gamma)$ as extrapolated to 0. The values of $c_2 = -0.1248$ and $c_3 = -0.359$ for both basis sets are in reasonable agreement with the theoretical values of $c_2 = -0.125$ and $c_3 = -0.4244$, which is taken as an indication that the method introduced in Sec. III provide a useful approximation method for the systems under consideration.

Results for 2s and 2p states are given in Table II. The spin-orbit coupling has been calculated in two different ways, the first one of which employs h_+'' in the variational procedure. The spin-orbit energy is calculated with the corresponding wave function and the operator $h_+ - h_+''$ as spin-orbit operator in first-order perturbation theory, as it is customary in fine-structure calculations with nonrelativistic wave functions and the Breit-Pauli spin-orbit coupling operator.⁹ The second method uses the full Hamiltonian h_+ including spin-orbit coupling. Both results

give good agreement with Dirac equation values as well as experimental results. Since the corrections of order γ^3 affect *s* and *p* states differently, the degeneracy of $s_{1/2}$ and $p_{1/2}$ states in the Dirac equation cannot be recovered.

In order to test the matrix representation with more realistic basis sets, a series of calculations with optimized exponents taken from the literature has been performed, the results of which are collected in Table III. Note that the bromine basis set has been optimized for the *N*-electron atom rather than for the highly ionized ion under consideration. The results are, however, in fair agreement with the large basis set calculation, especially for the uncontracted basis sets. In order to provide an estimate of the error of the matrix representation, again the results for h_+^{SOR} are given for the matrix method and for analytic evaluation of matrix elements. For the bromine basis set it is evident that for the contracted basis set the matrix error is relatively large (0.3%), whereas for the uncontracted basis set it has the same order of magnitude (1 part in 10^5) as the basis set error of the nonrelativistic calculation. For the iodine basis set, however, the accuracy of the total energies is about 1 part in 10^4 compared to 1 part in 10^5 for the nonrelativistic energy. These estimates of accuracy indicate that the total energies calculated with the matrix method are in error by about 1 part in 10^4 ; it remains

TABLE V. Bromine atom *r* expectation values in atomic orbitals (a.u.). Values in parentheses denote powers of 10.

<i>r</i>	Nonrelativistic	DHF	No-pair equation
1s	0.4367(-1)	0.4273(-1)	0.4214(-1)
2s	0.1936	0.1887	0.1886
3s	0.5592	0.5483	0.5478
4s	0.1742(1)	0.1709(1)	0.1719(1)
2p	0.1671	0.1666	0.1654
3p	0.5661	0.5652	0.5619
4p	0.2129(1)	0.2119(1)	0.2124(1)
3d	0.5829	0.5878	0.5836

TABLE VI. Bromine atom r^2 expectation values in atomic orbitals.

r^2	Nonrelativistic	DHF	No-pair equation
1s	0.2554(-2)	0.2459(-2)	0.2405(-2)
2s	0.4422(-1)	0.4205(-1)	0.4206(-1)
3s	0.3592	0.3453	0.3450
4s	0.3485(1)	0.3353(1)	0.3360(1)
2p	0.3302(-1)	0.3395(-1)	0.3346(-1)
3p	0.3744	0.3736	0.3691
4p	0.5318(1)	0.5266(1)	0.5297(1)
3d	0.4162	0.4258	0.4170

to be investigated whether the method yields valence shell excitation energies and properties of valence states that are sufficiently accurate to be compared with experiment.

V. MANY-ELECTRON ATOMS

A first study of this kind has been carried out for the bromine atom. A basis set of 47 contracted Gaussian functions which has been described in detail in Ref. 11 was used to construct a matrix representation of the spin-independent operator h_+'' . A standard Roothaan-type self-consistent-field (SCF) procedure was used to calculate molecular orbitals which are subsequently employed in a MRD-CI calculation from which the spin-orbit coupling of the ground state has been evaluated in first-order perturbation theory. In Tables IV–VI the results for the SCF calculation are collected and compared with nonrelativistic and DHF data.

The results show that h_+'' is capable of introducing relativistic effects in the charge distribution of a many-electron system. The values for orbital energies and the total energy are below those of the DHF calculation, partially because of the properties of h_+ discussed in Sec. V and partially because of the neglect of relativistic two-electron corrections. The valence-shell properties, however, are very close to the DHF result. From the expectation values of r and r^2 it can be seen that h_+'' correctly describes the relativistic contraction of s and p orbitals and the expansion of the d orbital, although the magnitude of this effect is larger for the DHF method.

The calculated spin-orbit coupling also shows that no-pair Hamiltonians provide a powerful tool for calculating relativistic effects, especially since the method can be easily generalized to molecules.

So it seems to be desirable to implement h_+ for molecular structure calculations. A possible way would be a generalization of the methods presented in Sec. III to the two-electron operators. Looking at (2.15) we find that this amounts to an effective four-index transformation of the two-electron integrals. This introduces, however, a further time-consuming step into the calculation unless it is combined with the transformation performed as well in a nonrelativistic calculation. A possible and very efficient way would encompass the use of molecular orbitals calculated with h_+'' as basis for a CI calculation employing h_+ . The required two-electron transformation could then be combined with the usual molecular-orbital transformation which is carried out before the CI calculation.

VI. SUMMARY

It has been found that no-pair Hamiltonians with free-particle projection operators can be used as Hamiltonian operators in an approximate relativistic two-component formalism for atomic and molecular structure calculations. The following properties of these operators are of particular importance in this context:

- (i) they can be derived from quantum electrodynamics;
- (ii) the binding energies for one-electron atoms agree to order $(Z\alpha)^2$ Ry with those of the Dirac equation, relativistic corrections are overestimated by an amount of order $(Z\alpha)^3$ Ry;
- (iii) they approach the correct nonrelativistic limit;
- (iv) the spin-orbit interaction and Breit interaction may be treated variationally;
- (v) no variational collapse is observed;
- (vi) no unphysical states occur.

The matrix method discussed in Sec. III has the following properties:

- (i) the model Hamiltonian approaches the correct nonrelativistic LCAO Hamiltonian for $c \rightarrow \infty$ for any basis set size (correct nonrelativistic limit of the matrix representation);
- (ii) it approaches the correct LCAO representation of h_+ for an infinitely large basis set for any value of c (limit of infinite basis set);
- (iii) the effort to implement the operator to atomic and molecular structure calculations is very low compared with four-component methods;
- (iv) if jj -coupled basis functions are used, no extra effort is required in the SCF-CI procedure.

Most interesting future developments would encompass

- (i) an explicit treatment of the two-electron operators;
- (ii) an attempt to evaluate the momentum-space operators directly in a basis set of Gaussian functions;
- (iii) the implementation of external field projection operators as suggested in Refs. 2 and 13.

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