Relativistic self-consistent-field calculations with the squared Dirac operator

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A four-component relativistic self-consistent-field scheme based on the squared Dirac operator is presented. Just as in the one-electron case, discussed previously [Chem. Phys. Lett. **78**, 341 (1981)], the variation principle holds and no variational collapse appears if the expansion method is applied. Numerical results with scalar Gaussian-lobe basis sets are given for He, Li, Be, H_2, and LiH.

I. INTRODUCTION

Interest in relativistic corrections to quantum-chemical descriptions of atoms and molecules during recent years[1-3] has stimulated the search for an appropriate relativistic many-electron Hamiltonian. The guideline has been to use as much as possible schemes and algorithms that are well established in nonrelativistic quantum chemistry.

Relativistic calculations based on the Hamiltonian

$$H(1,\ldots,N)=\sum_{i=1}^{N} D(i)+\sum_{\substack{i,j=1 \\ i<j}} \left[\frac{1}{r_{ij}}+B_{ij} \right] , \qquad (1)$$

with the Dirac operator D and Breit-type corrections B are now standard for atoms, at least in the self-consistent-field (SCF) approximation. Finite-difference methods have been used to solve the Dirac-Hartree-Fock (DHF) equations[4-13] (see Sec. II B)

$$H_{\text{eff}}\phi_i=\epsilon_i\phi_i , \quad i=1,2,\ldots,N .$$

The ϕ_i obtained in the DHF scheme are four-component spinors.

Some confusion had been caused by the so-called "Brown-Ravenhall disease." Brown and Ravenhall have shown[14] that the Hamiltonian (1) does not have discrete, bound eigenstates owing to the presence of continuum states with negative energies in the spectrum of the Dirac operator. However, various authors[15-19] have shown that this problem actually does not concern SCF calculations.

Unfortunately, a generalization of finite-difference methods for molecules is hardly possible. The only alternative, at present, seems to be the Roothaan expansion method, which has been applied to atoms[20-25] as well as molecules.[26,23,27-32] Most of these calculations have been done with so-called "scalar" basis sets, i.e., the same basis set was taken for all four components of the wave function, thus simplifying the integral evaluation for the matrix representation of the Hamiltonian.

However, in such calculations with the expansion method applied to the Dirac operator, a very unpleasant basis dependence called "variational collapse"[33] or "finite basis-set disease"[34] is observed, especially for molecules (see Appendix B). Given the Dirac operator

$$D =\beta mc^2+c\,\vec{\alpha}\cdot\vec{p}+V\mathbb{1}_{4\times4} , \qquad (2)$$

with

$$\beta=\begin{bmatrix} \mathbb{1}_{2\times2} & 0_{2\times2} \\ 0_{2\times2} & -\mathbb{1}_{2\times2} \end{bmatrix} , \quad \vec{\alpha}=\begin{bmatrix} 0_{2\times2} & \vec{\sigma} \\ \vec{\sigma} & 0_{2\times2} \end{bmatrix} , \qquad (3)$$

$\vec{\sigma}$ being the vector of Pauli spin matrices $\sigma_1,\sigma_2,\sigma_3$ and $\mathbb{1}_{n\times n}$ the n-dimensional unit matrix, one finds that the operator of kinetic energy $c\,\vec{\alpha}\cdot\vec{p}$ cannot be represented properly with a finite and hence incomplete basis set. Therefore, any finite matrix representation of the Dirac operator has states with wrong kinetic energy in its spectrum. Moreover, $c\,\vec{\alpha}\cdot\vec{p}$, in contrast to its nonrelativistic counterpart $p^2/2m$, is not bounded from below. Thus those unphysical states can contaminate the whole spectrum.

Recently Kutzelnigg[35] has explained the relation between the variational collapse and the wrong nonrelativistic limit of the Dirac operator's matrix representation. As a possible way to avoid the difficulties that arise from using the original Dirac operator, the many-electron (SCF) version of the squared Dirac operator is presented in Sec. II. Examples of numerical results for atoms and molecules are given in Sec. III. The quality of the wave functions calculated with the matrix representation of the squared Dirac operator is considered in Sec. IV. In Appendix A a special feature of the squared Dirac operator in connection with negative ions is discussed and in Appendix B an example for the variational collapse in molecules is given.

II. OUTLINE OF THE METHOD

A. The squared Dirac operator

An operator, whose matrix representation has the correct nonrelativistic limit, is obtained by squaring the original Dirac operator (2,3)

$$D\Psi=W\Psi ,$$

$$D^2\Psi=DW\Psi=W^2\Psi . \qquad (4)$$

To get rid of the constant rest-mass contribution, one defines

$$\Omega=\frac{D^2-m^2c^4}{2mc^2}=\frac{p^2}{2m}+\beta V+\frac{[\vec{\alpha}\cdot\vec{p},V]_+}{2mc}+\frac{V^2}{2mc^2} \qquad (5)$$

and, with $W = E + mc^2$,

$$\Omega\Psi = \frac{W^2 - m^2c^4}{2mc^2}\Psi = \left[E + \frac{E^2}{2mc^2}\right]\Psi = \omega\Psi . \tag{6}$$

The nonrelativistic limit $(c \to \infty)$ is given by the first two terms on the right-hand side of (5). It is exactly the non-relativistic Hamiltonian for the upper components of Ψ and a "positron Hamiltonian" $(p^2/2m - V)$ for the lower components, reflecting the identity of positron and hole states in the nonrelativistic limit.

Ω is, like D^2, bounded from below (see Fig. 1). The variation principle can hence be applied without taking any special precautions. This has been done successfully for one-electron systems by means of the matrix representation in scalar basis sets of Gaussian-lobe functions.[36]

B. A relativistic SCF scheme based on Ω

In the DHF scheme the wave function usually is taken as an antisymmetrized product of four-component one-electron spinors

$$\Psi = |\phi_1(1)\phi_2(2) \cdots \phi_N(N)| . \tag{7}$$

Kramer's restriction[37] could be imposed, in principle, but will not be regarded in the following for simplicity.

The ϕ_i together with the corresponding spinor energies ϵ_i can be obtained from (see Introduction)

$$D_{\text{eff}}\phi_i = \epsilon_i\phi_i , \quad i = 1,2,\ldots,N , \tag{8}$$

with

$$D_{\text{eff}} = \beta mc^2 + c\,\vec{\alpha}\cdot\vec{p} + V + G \tag{9}$$
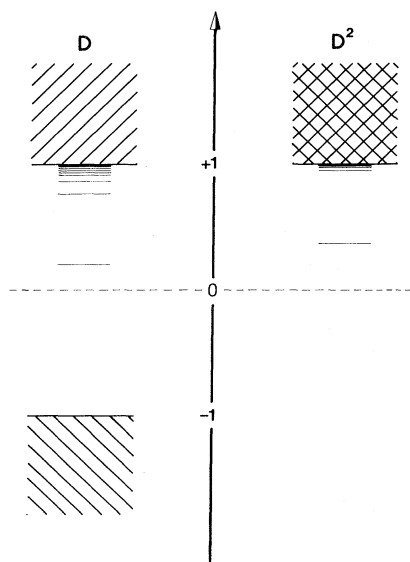
and

$$G = \sum_j^N (J_j - K_j) , \tag{10}$$

FIG. 1. Schematic representation of the spectra of Dirac operator and squared Dirac operator. The eigenvalues of D/mc^2 and D^2/m^2c^4 are given in units of mc^2.

J and K being the relativistic analogs of Coulomb and exchange operators in nonrelativistic SCF theory. Relativistic corrections to the electron interaction, e.g., the Breit interaction, can be included, too.

To solve the DHF equations (8) one can apply the concept of Ω, defining

$$\Omega_{\text{eff}} = \frac{D_{\text{eff}}^2 - m^2c^4}{2mc^2}$$

$$= \frac{p^2}{2m} + \frac{[\beta,(V+G)]_+}{2} + \frac{[\vec{\alpha}\cdot\vec{p},(V+G)]_+}{2mc}$$

$$+ \frac{(V+G)^2}{2mc^2} . \tag{11}$$

It should be noted that β and K do not commute in the relativistic case. Actually they anticommute since K couples upper and lower components of the ϕ_i.

In contrast to the original DHF equations, the set of equations

$$\Omega_{\text{eff}}\phi_i = \omega_i\phi_i , \quad i = 1,2,\ldots,N \tag{12}$$

does not show the variational collapse on expansion in a finite basis set. The spinor energies ϵ_i can be calculated from the ω_i by

$$\epsilon_i = -mc^2 + \sqrt{m^2c^4 + 2mc^2\omega_i} \tag{13}$$

and the total SCF energy is given as

$$E_{\text{RSCF}} = \sum_i^N (\epsilon_i - \tfrac{1}{2}\langle\phi_i \,|\, G \,|\, \phi_i\rangle) . \tag{14}$$

There is no other simple relation for the SCF energy because, in general,

$$\langle D_{\text{eff}}^2\rangle \neq \langle D_{\text{eff}}\rangle\langle D_{\text{eff}}\rangle .$$

The nonrelativistic limit of Ω_{eff} is

$$\Omega_{\text{eff}}^{nr} = \frac{p^2}{2m} + \beta(V+G) . \tag{15}$$

Again, for the upper components this is exactly the nonrelativistic Fock operator, whereas for the lower components the sign of the potential is changed. Since G no longer couples upper and lower components, it commutes with β.

The last term in Eq. (11) contains the square of the electron interaction operator. From (10) one has

$$G^2 = \sum_{k,1}^N (J_k - K_k)(J_1 - K_1) . \tag{16}$$

The evaluation of matrix elements of G^2 would involve the calculation of three-electron integrals (the four-electron integrals factorize into two-electron integrals). This can be circumvented if one forms G^2 from the matrix representation of G, assuming that a completeness relation holds. The error thus introduced affects the energy only in $O(c^{-2})$. It has been shown already for the one-electron case[36] that the results do not change significantly if the products of V are formed with the respective matrix representations and not on the operator level. For small

TABLE I. He atom, ground-state energies and expectation values. All values given in Hartree units.

Basis	This work (Ω)		Other authors (original D)		
	$4s/4p^{a}$	$11s/11p^{a}$	DHF[b]	RSCF/Slater[c]	RSCF/Gauss[d]
E_{SCF}^{nr}	-2.84675	-2.86164	-2.86168	-2.86168	-2.86166
ΔE_{SCF}^{rel}	-0.00007	-0.00013	-0.00013	-0.00016	-0.00015
$\epsilon_{1s_{1/2}}^{nr}$	-0.907030	-0.917942	-0.917954	-0.91796	-0.917949
$\Delta\epsilon_{1s_{1/2}}^{rel}$	-0.000014	-0.000034	-0.000037	$+0.00007$	-0.000042
$\langle J-K\rangle^{nr}$	1.03269	1.02576	1.02577		1.02576
$\Delta\langle J-K\rangle^{rel}$	0.00004	0.00006	0.00006		0.00007

[a]Basis sets are given in Table VIII.

[b]From Ref. 11, finite difference integration of the Dirac-Hartree-Fock equations.

[c]From Ref. 20, relativistic SCF calculation with the Roothaan expansion method. Slater-type functions with noninteger main quantum number were used to expand the radial parts of the spinors.

[d]From Ref. 29, relativistic SCF calculation with the Roothaan expansion method in a basis of Gaussian-lobe functions ($11s/11p$).

nuclear charges Z the expectation value $\langle V\rangle$ is of $O(Z^2)$, whereas $\langle G\rangle$ only of $O(Z)$. The situation should thus even be better for G than for V.

The same argument holds, of course, for $[\vec{\alpha}\cdot\vec{p},(V+G)]_{+}$. The matrix representation of $[\vec{\alpha}\cdot\vec{p},G]_{+}$ can be obtained from the matrix representations of $\vec{\alpha}\cdot\vec{p}$ and G. Just like $\vec{\alpha}\cdot\vec{p}$ itself, the anticommutator couples upper and lower components of the ϕ_i, the latter being of $O(c^{-1})$. Together with the coefficient $1/(2mc)$ a contribution to the energy of $O(c^{-2})$ is found, too. Computational details are given in Sec. III.

III. NUMERICAL CALCULATIONS

Relativistic SCF calculations of some small atoms and molecules have been performed by means of Eqs. (11)–(14) with scalar basis sets of Gaussian-lobe functions. In particular, the matrix representations of $[\vec{\alpha}\cdot\vec{p},V]_{+}$ and V^2 have been calculated exactly, whereas those of $[\vec{\alpha}\cdot\vec{p},G]_{+}$, $[VG]_{+}$, and G^2 have been formed as

matrix products. The results are given in Tables I–VII. In Tables VIII and IX the basis sets are listed.

A. Results for atoms

For He (Table I) and Be (Table II) the results are very close to the DHF values of Desclaux,[11] calculated with a finite-difference method. In contrast to calculations with the matrix representation of the original Dirac operator,[29] the results obtained with Ω have a systematic basis dependence, i.e., extension of the basis set always gives a lower energy. This is certainly due to the fact that Ω is bounded from below.

The results for the ground state of the Li atom (Table III) show a splitting of the $1s_{1/2}$ level into the $m_j=+\frac{1}{2}$ and $m_j=-\frac{1}{2}$ sublevels. This is a consequence of the unrestricted ansatz for the wave function. If one chooses the one-electron spinors as eigenfunctions of $\vec{j}=\vec{l}+\vec{s}$ the interaction between electrons is found to depend on

TABLE II. Be atom, ground-state energies and expectation values. All values in Hartree units.

Basis	This work (Ω)		Other authors (original D)	
	$8s/8p^{a}$	$14s/14p^{b}$	DHF[c]	RSCF/Slater[d]
E_{SCF}^{nr}	-14.5607	-14.5728	-14.5730	-14.5730
ΔE_{SCF}^{rel}	-0.0025	-0.0028	-0.0029	-0.0029
$\epsilon_{1s_{1/2}}^{nr}$	-4.75047	-4.73259	-4.73269	-4.73267
$\Delta\epsilon_{1s_{1/2}}^{rel}$	-0.00067	-0.00081	-0.00081	-0.00082
$\epsilon_{2s_{1/2}}^{nr}$	-0.312223	-0.309260	-0.309270	-0.30927
$\Delta\epsilon_{2s_{1/2}}^{rel}$	-0.000048	-0.000052	-0.000053	-0.00005
$\langle J-K\rangle^{nr}$	4.43530	4.48910		
$\Delta\langle J-K\rangle^{rel}$	0.00103	0.00110		

[a]Basis sets are given in Tables VIII and IX.

[b]See Table IX, contraction: [4,10∗1/4,10∗1]. The first four s and p functions had fixed coefficients, the remaining ten s and p functions were uncontracted.

[c]See Table I, footnote b.

[d]See Table I, footnote c.

TABLE III. Li atom, ground-state energies and expectation values. All values in Hartree units.

Basis	This work (Ω)		Original D
	$9s/9p^a$	$14s/14p^b$	DHF^c (restricted)
E_{SCF}^{nr}	−7.429 58	−7.432 65	−7.432 73
ΔE_{SCF}^{rel}	−0.000 78	−0.000 79	−0.000 80
$\epsilon_{1s_{1/2}}^{nr}(m_j=+\frac{1}{2})$	−2.485 52	−2.486 65	−2.477 73
$\epsilon_{1s_{1/2}}^{nr}(m_j=-\frac{1}{2})$	−2.468 35	−2.468 67	
$\Delta\epsilon_{1s_{1/2}}^{rel}(m_j=+\frac{1}{2})$	−0.000 25	−0.000 24	−0.000 25
$\Delta\epsilon_{1s_{1/2}}^{rel}(m_j=-\frac{1}{2})$	−0.000 25	−0.000 23	
$\epsilon_{2s_{1/2}}^{nr}(m_j=+\frac{1}{2})$	−0.195 057	−0.196 363	−0.196 323
$\Delta\epsilon_{2s_{1/2}}^{rel}(m_j=+\frac{1}{2})$	−0.000 013	−0.000 016	−0.000 016
$\langle J-K\rangle^{nr}$	2.280 92	2.280 96	
$\Delta\langle J-K\rangle^{rel}$	0.000 27	0.000 31	

^{a}Basis sets are given in Tables VIII and IX.
^{b}See Table IX, contraction: [4,10*1/4,10*1].
^{c}See Table I, footnote b.

the m_j values (projection of $\vec{j}$ onto the axis of quantization) of the respective spinors, according to their symmetry. For example, there is no exchange interaction between $s_{1/2}(m_j=+\frac{1}{2})$ and $s_{1/2}(m_j=-\frac{1}{2})$ spinors. Thereby, the two $1s$ electrons of Li are no longer equivalent, since only one of the $1s_{1/2}$ spinors can have the same m_j value as the $2s_{1/2}$ spinor. This situation can be regarded as an example of spin polarization. The calculated SCF wave function turns out to be a linear combination of a ^2S and a ^4S state. Nevertheless, the relativistic contribution to the total energy of the Li atom is not affected significantly by spin polarization, as can be seen by comparison with the (restricted) DHF result.

B. Results for molecules

Numerical calculations of molecules based on the original Dirac operator may suffer very seriously from the

TABLE IV. H$_2$ molecule, ground-state energies and expectation values. Energies in Hartree units, bond lengths in Bohr units.

Basis	This work (Ω) $7s/7p^e$	Orig. D^a	$D^a/c\to\infty^b$	$D^c/c\to\infty^b$ $6s/5p$	Pert. theory^d
		$5s/5p/1d$			
R(H-H)	1.3959^f	1.4011^g		1.40^g	1.4011^g
E_{SCF}^{nr}	−1.130 485 3	−1.132 221	−1.133 106	−1.117 690	−1.174 474 6
ΔE_{SCF}^{rel}	−0.000 012 2	−0.000 898	−0.000 014	−0.000 014	−0.000 010 9
$\epsilon_{1s\sigma_{g1/2}}^{nr}$	−0.594 889 2	−0.594 004 9	−0.594 313 6	−0.589 95	
$\Delta\epsilon_{1s\sigma_{g1/2}}^{rel}$	−0.000 003 1	−0.000 312 4	−0.000 003 7	−0.000 01	
$\langle J-K\rangle^{nr}$	0.657 071 2	0.657 913 1	0.658 179 7		
$\Delta\langle J-K\rangle^{rel}$	0.000 006 0	0.000 273 3	0.000 006 6		
D_e^{nr}	0.133 104 9				
ΔD_e^{rel}	0.000 000 4				
$D_e^{nr}(cp)^h$	0.132 811 4				
$\Delta D_e^{rel}(cp)^h$	0.000 000 4				

^{a}From Ref. 29, see footnote d, Table I.
^{b}Nonrelativistic reference calculated by substituting for the lower components and setting $c\to\infty$.
^{c}From Ref. 27, relativistic SCF calculation with the original Dirac operator. Different basis sets of spherical Gaussian-type functions have been used for upper and lower components of the molecular spinors.
^{d}From Ref. 39, first-order perturbation theory (Pauli approx.) with an explicitly correlated wave function. The nonrelativistic reference is not an SCF energy.
^{e}Basis set given in Table VIII, contraction: [2,5*1/2,5*1].
^{f}Nonrelativistic equilibrium bond length for the basis given.
^{g}Experimental bond length.
^{h}Counterpoise-corrected values (see Sec. III B).

TABLE V. LiH molecule, (a) ground-state energies and expectation values. Energies in Hartree units, bond lengths in Bohr units. (b) Dissociation energies. All values in Hartree units.

(a)

		This work (Ω)	$D/c \to \infty^{a}$
Li	$9s/9p^{b}$		$12s/8p$
Basis			
H	$7s/7p^{c}$		$4s/2p$
R^{nr}(Li-H)		3.0403^{d}	3.0140^{e}
E_{SCF}^{nr}		$-7.981\,463$	$-8.059\,21$
ΔE_{SCF}^{rel}		$-0.000\,797$	$-0.000\,83$
$\epsilon_{1\sigma}^{nr}$		$-2.452\,811$	$-2.575\,61$
$\Delta\epsilon_{1\sigma_{1/2}}^{rel}$		$-0.000\,249$	
$\epsilon_{2\sigma_{1/2}}^{nr}$		$-0.299\,869\,1$	$-0.312\,72$
$\Delta\epsilon_{2\sigma_{1/2}}^{rel}$		$-0.000\,011\,7$	$0.000\,00$
$\langle J-K \rangle^{nr}$		$3.463\,110$	
$\Delta\langle J-K \rangle^{rel}$		$0.000\,275$	
ΔR^{rel}(Li-H)^{f}		-0.0003	

(b)

Covalent (LiH$\to$Li+H)

D_{e}^{nr}	$0.053\,192$
ΔD_{e}^{rel}	$0.000\,014$
$D_{e}^{nr}(cp)^{g}$	$0.052\,741$
$\Delta D_{e}^{rel}(cp)^{g}$	$0.000\,012$

Ionic (LiH$\to$Li^{+}+H^{-})

D_{e}^{nr}	$0.260\,220$
ΔD_{e}^{rel}	$0.000\,029$

[a]From Ref. 28, see footnotes b and c, Table IV.
[b]Basis set given in Table VIII, contraction: [2,5*1/2,5*1].
[c]Basis set given in Table VIII, contraction: [3,4*1/3,4*1].
[d]Nonrelativistic bond length for the basis given.
[e]Experimental bond length.
[f]Relativistic bond contraction, see explanations in the text.
[g]Counterpoise corrected (see Sec. III B).

TABLE VI. Li^{+} and H^{-} atom, ground-state energies and expectation values. All values in Hartree units.

Atom Basis	Li^{+} $9s/9p^{a}$	H^{-} $7s/7p^{a}$
E_{SCF}^{nr}	$-7.234\,552$	$-0.486\,691\,1$
ΔE_{SCF}^{rel}	$-0.000\,763$	$-0.000\,004\,6$
$\epsilon_{1s_{1/2}}^{nr}$	$-2.790\,983$	$-0.043\,847\,6$
$\Delta\epsilon_{1s_{1/2}}^{rel}$	$-0.000\,259$	$-0.000\,000\,4$
$\langle J-K \rangle^{nr}$	$1.652\,587$	$0.398\,996\,0$
$\Delta\langle J-K \rangle^{rel}$	$0.000\,245$	$0.000\,004\,0$

[a]Basis sets given in Table VIII.

variational collapse. The mixing of physical and unphysical solutions can produce very poor results in calculations with small basis sets. Even for linear molecules d-type basis functions are needed to describe σ-type spinors and f-type basis functions for π-type spinors if one wants to have the correct order of magnitude in the relativistic contributions to the energy[36,38] (see Appendix B).

In contrast, the matrix representation of Ω needs no extra basis functions of higher angular momentum. The calculations of molecules reported in this paper have all been done with basis sets composed of purely atomic basis sets. Since scalar basis sets offer the same functions for all components of the wave function, those functions which are needed to describe the lower components of the atomic spinors serve to polarize the upper components of molecular spinors, and vice versa.

Owing to limitations in core-memory size of the computers used, the basis sets for the molecules (as well as the large ones for the atoms) had to be contracted, i.e., the coefficients of the basis functions with the highest exponents were kept fixed during the calculations. The contraction coefficients (see Table VIII) have been taken from calculations of the separate atoms.

TABLE VII. Relativistic SCF energies, expectation values of the DHF operator and virial quotients for He, Li, Be, H$_2$, and LiH. All energies in Hartree units.

System	E_{RSCF}^{a}	$\langle D_{eff} \rangle^{b}$	q_1^{c}	q_2^{d}	Basis^{e}
He	$-2.846\,82$	$-2.858\,27$	$0.998\,967$	$0.993\,934$	$4s/4p$
	$-2.861\,77$	$-2.861\,79$	$1.000\,016$	$1.000\,023$	$11s/11p$
Li	$-7.430\,36$	$-7.486\,31$	$1.013\,487$	$1.019\,468$	$9s/9p$
	$-7.433\,44$	$-7.433\,49$	$1.000\,019$	$1.000\,031$	$14s/14p$
Be	-14.5632	-14.5921	$1.000\,793$	$0.999\,599$	$8s/8p$
	-14.5756	-14.5758	$1.000\,015$	$1.000\,021$	$14s/14p$
H$_2$	$-1.130\,498$	$-1.134\,408$	$1.003\,497$	$1.003\,495$	$7s/7p$
LiH	$-7.982\,260$	$-8.025\,694$	$1.007\,512$	$1.009\,564$	f

[a]Relativistic SCF energy calculated with Ω_{eff}, see Eqs. (11)-(14).
[b]Expectation value of $D_{eff}=\beta'mc^2 +c\,\vec{\alpha}\cdot\vec{p}+V+ \sum_j (J_j-K_j)$ with the wave function obtained from Ω_{eff}; $\beta'=\beta-1$.
[c]$q_1 = -\langle V+ \sum_j (J_j-K_j)\rangle /\langle c\,\vec{\alpha}\cdot\vec{p}\rangle$, V contains the nuclear repulsion; see Sec. IV.
[d]$q_2 =E_{RSCF}/\langle \beta'mc^2 \rangle$; see Sec. IV.
[e]See Tables VIII and IX.
[f]Li:$9s/9p$, H:$7s/7p$.

TABLE VIII. Exponents and contraction coefficients of Gaussian-lobe basis sets for H, He, Li, and Be.

Atom designation	s-type functions		p-type functions	
	Contraction coefficients	Exponents	Contraction coefficients	Exponents
H	0.005 517	1293.70	0.0677	1681.81
7s /7p	0.061 569	196.000	0.2348	254.800
	0.554 750	29.7000	0.9678	38.6100
He		4.500 38		5.850 49
		0.681 277		0.885 660
		0.151 374		0.196 786
		0.034 000		0.044 000
He		117.000		181.765
4s /4p		13.6232		17.7102
		1.998 94		2.598 63
		0.382 938		0.497 819
Be		4360.00		6233.43
8s /8p		438.000		779.178
		74.2075		111.311
		16.8753		25.3129
		4.646 75		6.970 12
		1.406 95		2.110 42
		0.281 390		0.422 096
		0.056 277 9		0.084 416 9
Li	0.0734	86 979.3	0.0318	173 959.0
(9s /9p)	0.9637	9685.89	0.1417	19 371.8
		1294.90		2589.81
		207.850		415.700
		40.0481		80.0963
		9.028 71		18.0574
		2.433 00		4.866 00
		0.710 627		1.421 26
		0.047 789 3		0.095 578 6
He		279 951.0[a]		
(11s /11p)		35 891.1		
		4984.88		
		755.285		
		124.505		
		28.0994		
		7.921 66		
		2.580 74		
		0.918 171		
		0.347 207		
		0.137 777		

[a]The same exponents have been taken for s- and p-functions.

For H_2 as well as for LiH, a nonrelativistic potential curve was calculated to find the nonrelativistic equilibrium bond lengths for the respective basis set. In addition, for LiH a symmetric pattern of five different internuclear distances, including the nonrelativistic equilibrium value, was examined to obtain an estimate of the relativistic correction to the bond length.

The results for H_2 are given in Table IV. For comparison, results of other authors are included. There is an excellent agreement in the relativistic correction to the total energy between the Ω result and the perturbational result of Kolos and Wolniewicz,[39] taking into account that the latter was obtained with an explicitly correlated wave function. The results of Mark and Rosicky[29] have been obtained with the original Dirac operator and a scalar basis set comparable to those used in this paper. A

TABLE IX. $14s/14p$ Gaussian-lobe basis sets for Li and Be.

Li			Be		
Contraction coefficients			Contraction coefficients		
s	p	Exponents	s	p	Exponents
0.0003	0.0106	737 726.0	0.0005	0.0017	1 035 170.0
0.0046	0.0452	87 824.5	0.0047	0.0060	147 882.0
0.0499	0.1982	11 555.9	0.0511	0.0267	21 126.0
0.5534	0.8034	1699.39	0.5744	0.1112	3018.00
		280.136			498.020
		63.2235			112.397
		17.8237			31.6866
		5.806 66			10.3230
		2.065 89			3.672 68
		0.781 216			1.388 83
		0.309 998			0.551 108
		0.123 999			0.211 965
		0.049 599 7			0.078 505 4
		0.019 839 9			0.028 037 7

reasonable relativistic correction was found only by means of the so-called "high c" approximation, i.e., by defining the correction in relation to the actual nonrelativistic limit of the matrix representation of the Dirac operator. In a similar way the results of Matsuoka et al.[27] have been obtained.

The lower bound of Ω allows to look at quantities other than the total energy. For example, one finds that the relativistic correction to the dissociation energy is even an order of magnitude smaller than the correction to the total energy of a single hydrogen atom. To exclude artifacts of the basis set, the dissociation energy has also been determined with respect to H atoms calculated with the basis set of the whole molecule (counterpoise correction). Obviously the relativistic correction to the dissociation energy is not changed and can thus be regarded as being significant. The invariance against the counterpoise correction is not surprising since the relativistic details of an atomic wave function cannot be improved very much by basis functions located "outside" the atom, i.e., far away from the nucleus.

Clearly, for LiH relativistic corrections are much more pronounced [Table V (a)]. The results roughly agree with those of Aoyama et al.,[28] which have been obtained at the experimental bond length. This bond length differs considerably from the equilibrium value obtained in this work. Therefore, a large influence of electron correlation is to be expected. As electron correlation tends to reduce the ionic character of the Li-H bond, a reduction of charge density at the hydrogen nucleus, together with a shortening of the bond length, is very likely to enlarge the relativistic corrections.

By the procedure described above, a relativistic bond contraction of 0.010% was found, which fits very well into the rule of thumb of Pyykkö and Desclaux[3] predicting 0.008%. There are also certain parallels to H_2. For example, although the relativistic correction to the co-

valent dissociation energy [Table V (b)] is much larger than for H_2, it is, just as for H_2, 3 orders of magnitude smaller than the correction to the total energy. Also for LiH the correction to the dissociation energy is nearly not modified by the counterpoise correction.

The ionic dissociation energy of LiH [LiH $\rightarrow$ $Li^+ + H^-$, Table V (b)] is, of course, much larger and has a relativistic correction twice as large as the covalent one. The difference between both corrections is roughly equal to the relativistic correction to the $2s_{1/2}$ spinor energy of the Li atom (see Table III). It thus should be due to the transfer of an electron from the "slightly" relativistic H nucleus (see Table VI) into the influence of the Li nucleus on forming the LiH molecule from Li^+ and H^-.

IV. QUALITY CONSIDERATIONS

In a complete basis set eigenfunctions of $\Omega_{\rm eff}$ are eigenfunctions of $D_{\rm eff}$ as well. Accordingly, the expectation value of $D_{\rm eff}$ with an eigenfunction of $\Omega_{\rm eff}$ should be close to the SCF energy calculated from the ω_i [see Eqs. (12)—(14)]. Table VII contains these values for the atoms and molecules, discussed in Sec. III.

For He, Li, and Be, $E_{\rm RSCF}$ and $\langle D_{\rm eff} \rangle$ do not agree very well in the small basis sets. Obviously $\langle D_{\rm eff} \rangle$ tends to overestimate the relativistic contributions to the SCF energies. This is not surprising since $D_{\rm eff}$ is not bounded from below. For the large basis sets, however, there is no considerable difference between both kinds of values. They can hence be expected to converge to the same limit with increasing size of the basis set. The wave functions then become eigenfunctions of $\Omega_{\rm eff}$ and $D_{\rm eff}$ at the same time.

Similar information can be taken from the relativistic virial theorem.[20] For atoms and molecules one has

$$W = E + mc^2 = \langle \beta mc^2 \rangle + \langle c\, \vec{\alpha} \cdot \vec{p} \rangle + \langle V \rangle$$

or

$$E = \langle \beta' mc^2 \rangle + \langle c \vec{\alpha} \cdot \vec{p} \rangle + \langle V \rangle \ ,$$

with

$$\beta' = \beta - 1_{4 \times 4} = \begin{bmatrix} 0_{2 \times 2} & 0_{2 \times 2} \\ 0_{2 \times 2} & 21_{2 \times 2} \end{bmatrix} .$$

The nuclear repulsion has to be included in V if one has molecules in their equilibrium geometry. For the exact wave function

$$\langle c \vec{\alpha} \cdot \vec{p} \rangle = - \langle V \rangle \ ,$$

such that

$$W = \langle \beta mc^2 \rangle$$

and

$$E = \langle \beta' mc^2 \rangle \ .$$

For an approximate wave function the quotients

$$Q_1 = - \frac{\langle V \rangle}{\langle c \vec{\alpha} \cdot \vec{p} \rangle}$$

and

$$Q_2 = \frac{E}{\langle \beta' mc^2 \rangle}$$

or, in the SCF scheme (see Sec. II B),

$$q_1 = - \frac{\langle V + G \rangle}{\langle c \vec{\alpha} \cdot \vec{p} \rangle}$$

and

$$q_2 = \frac{E_{RSCF}}{\langle \beta' mc^2 \rangle}$$

should be as close as possible to unity. G is the electron interaction (10) and E_{RSCF} the relativistic SCF energy according to Eqs. (12)–(14). The quotients q_1 and q_2 are listed in Table VII, too.

Again, for the large basis sets good results are found. Both versions of the relativistic virial theorem are fulfilled. The deviations for the small basis sets, however, have two different aspects.

On the one hand, the wave function obtained from Ω does not reproduce correctly the relation between kinetic, potential, and rest-mass energy that is to be expected for eigenfunctions of the Dirac operator. This is equivalent to the finding that E_{RSCF} and $\langle D_{eff} \rangle$ do not agree (see above), showing that the wave functions obtained are not eigenfunctions of the Dirac operator.

On the other hand, $\beta' mc^2$, $c \vec{\alpha} \cdot \vec{p}$, and V or $V + G$, respectively, are no explicit parts of Ω (11) but constituents of the operator products contained in Ω. Thereby, errors in the matrix representation of the Dirac operator are not automatically contained in the matrix representation of Ω. Owing to the variational collapse, deficiencies of the basis set are much more critical for the Dirac operator than for Ω. This makes q_1 and q_2 very sensitive parameters for the saturation of the basis set.

For H_2 and LiH only comparatively small basis sets could be taken (see q_1 and q_2). Nevertheless, satisfactory SCF energies and relativistic corrections have been obtained by means of Ω_{eff}. According to $\langle D_{eff} \rangle$ the wave functions obtained from Ω differ considerably from those that would have been obtained from the original Dirac operator (see Appendix B), since there is no variational collapse for Ω.

V. CONCLUSIONS

The validity of the variation principle for Ω, which has been documented previously for one-electron systems,[36] is maintained in an SCF scheme based on Ω. Calculations with scalar basis sets do not suffer from the variational collapse and can thus be performed in a straightforward manner, much like in nonrelativistic quantum chemistry. The lower-bound property and the correct nonrelativistic limit of the matrix representation of Ω allow to calculate even very small relativistic corrections.

The additional operators that are contained in Ω are no trouble in practical calculations, especially if a parallel computer is employed. Vectorization of the Ω-based SCF program on the CYBER 205 of the Rechenzentrum der Ruhr-Universität Bochum is in progress and can be done even more efficiently than for a nonrelativistic SCF program.

Alternative modifications of the Dirac operator that can be used for SCF calculations have been proposed by Mark and Schwarz,[40] by Kutzelnigg,[35] and by Wallmeier and Kutzelnigg.[41] Nevertheless, of all the operators proposed, Ω is still the only one which is bounded from below. Future calculations will show which modification is best suited for many-electron systems, especially in connection with a relativistic CI scheme.

ACKNOWLEDGMENTS

APPENDIX A: REMARK ON THE SPECTRUM OF Ω

The spectrum of Ω contains a continuum where particle and hole states are degenerate (see Fig. 1). As a consequence, linear combinations of particle and hole states can be eigenstates of Ω but not of the original Dirac operator. In principle, this fact can raise complications if weakly bound electrons are present. A good example for that situation should be the H^- atom.

Table X shows the lowest ten Hartree-Fock spinor energies of H^- from a relativistic SCF calculation with Ω in a $7s/7p$ Gaussian-lobe basis set (see Table VIII). Obviously the ground-state spinors $(1s_{1/2})$ do not have the lowest spinor energies. There is a set of spinors that have energies below those of the ground-state spinors. On inspection they are identified as hole states, i.e., they have large

TABLE X. H^- atom, spinor energies from a SCF calculation with Ω in $7s/7p$ Gaussian-lobe basis (see Table VII). All energies in Hartree units. Expectation values of r^2 in (Bohr units)^2.

j	degeneracy	ϵ	$\langle r^2 \rangle$	
$\frac{1}{2}$	2	$-0.166\,568\,6$	21.5173	
$\frac{1}{2}$	2	$-0.090\,356\,2$	28.6805	hole states
$\frac{3}{2}$	4	$-0.090\,355\,1$	28.6806	
$\frac{1}{2}$	2	$-0.043\,847\,8$	8.6425	particle states[a]

[a] $1s_{1/2}$ SCF ground-state spinors.

lower and negligible upper components. At first glance this looks like a contradiction to the lower bound of Ω.

To clarify the situation one has to keep in mind the correspondence between Dirac holes and positrons. In the SCF calculation the hole states have been treated as virtual spinors for which Ω does not distinguish between holes and positrons. Compared to the H atom, the virtual hole states get a lower energy under the influence of the negative charge of the H^- atom. This situation, which actually is an artifact of Ω, is valid only as long as the hole states are unoccupied.

Putting a positron in one of the virtual hole states with spinor energies lower than those of the electronic ground-state spinors does not necessarily lead to a total energy of the $(2e^-, 1e^+)$ atom, which is lower than that of the H^- atom, i.e., to a bound positron. The repulsive interaction between the nucleus and the positron will change the picture drastically. To what extent the attractive interaction with the electrons is compensated can only be figured out by a calculation of the $(2e^-, 1e^+)$ atom.

A real mixing of particle and hole states was not observed. All eigenspinors could definitely be classified as either particle or hole.

APPENDIX B: VARIATIONAL COLLAPSE IN A DIATOMIC, HOMONUCLEAR ONE-ELECTRON MOLECULE

For molecules the variational collapse of the Dirac operator leads to a mixing of physical and unphysical states if they have the same symmetry and degenerate or near-degenerate energies. The unphysical states are generated by the inappropriate matrix representation of the kinetic energy operator $c\,\vec{\alpha}\cdot\vec{p}$. They are characterized by a wrong relation between upper and lower components of the respective spinors. As an example, the ground-state spinor of the H_2^+ molecule is considered. According to the formalism of molecular spinors from linear combinations of atomic orbitals (LCAO-MS),[42] it is called $1s\sigma_{g1/2}$, being a linear combination of two $1s_{1/2}$ atomic spinors [see Table XI (a)].

The corresponding eigenspinor of the matrix representation of the Dirac operator in a basis of Gaussian-lobe functions (s and p type only) is given in Table XII (a). One can see that there are contributions not belonging to the $s\sigma_{g1/2}$ symmetry. For example, the upper components

TABLE XI. Schematic representation of a $s\sigma_{g1/2}$ and a $p\sigma_{g1/2}$ spinor for a homonuclear diatomic molecule as linear combination of atomic spinors.

(a)

$$\varphi_{ns_{1/2}}^{m_j=+1/2} = \begin{bmatrix} N_1 s \\ 0 \\ iN_3 p_z \\ iN_4(p_x + ip_y) \end{bmatrix} \rightarrow \varphi_{ms\sigma_{g1/2}}^{m_j=+1/2} = \begin{bmatrix} M_1(s_A + s_B) \\ 0 \\ iM_3(p_{zA} + p_{zB}) \\ iM_4(p_{xA} + ip_{yA} + p_{xB} + ip_{yB}) \end{bmatrix}$$

(b)

$$\varphi_{n'p_{1/2}}^{m_j=+1/2} = \begin{bmatrix} N_1' p_z \\ N_2'(p_x + ip_y) \\ -iN_3' s \\ 0 \end{bmatrix} \rightarrow \varphi_{m'p\sigma_{g1/2}}^{m_j=+1/2} = \begin{bmatrix} M_1'(p_{zA} - p_{zB}) \\ M_2'(p_{xA} + ip_{yA} - p_{xB} - ip_{yB}) \\ -iM_3'(s_A - s_B) \\ 0 \end{bmatrix}$$

n, n': atomic main quantum numbers; N, N', M, M': normalization factors; A, B: atom indices.

TABLE XII. Dirac eigenspinor for the ground state of H_2^+ in a Gaussian-lobe basis set of (a) s and p functions and (b) s, p, and d functions. Type designations: $0=s$, $1=p_x$, $2=p_y$, $3=p_z$, $11=d_{xy}$, $12=d_{xz}$, $13=d_{yz}$, $14=d_{x^2-y^2}$, $15=d_{z^2}$ function.

(a)

Atom	Type	Component 1 Real	Component 1 Imaginary	Component 2 Real	Component 2 Imaginary	Component 3 Real	Component 3 Imaginary	Component 4 Real	Component 4 Imaginary
1	0	0.003785	0.0	0.0	0.0	0.0	−0.000002	0.0	0.0
1	0	0.053604	0.0	0.0	0.0	0.0	−0.000010	0.0	0.0
1	0	0.304583	0.0	0.0	0.0	0.0	−0.000601	0.0	0.0
1	0	0.219998	0.0	0.0	0.0	0.0	−0.005434	0.0	0.0
1	1	0.0	0.0	−0.004280	0.0	0.0	0.0	0.0	0.000096
1	1	0.0	0.0	0.037693	0.0	0.0	0.0	0.0	0.000374
1	1	0.0	0.0	−0.125400	0.0	0.0	0.0	0.0	0.001259
1	1	0.0	0.0	0.057528	0.0	0.0	0.0	0.0	0.000217
1	2	0.0	0.0	0.0	−0.004280	0.0	0.0	−0.000096	0.0
1	2	0.0	0.0	0.0	0.037693	0.0	0.0	−0.000374	0.0
1	2	0.0	0.0	0.0	−0.125400	0.0	0.0	−0.001259	0.0
1	2	0.0	0.0	0.0	0.057528	0.0	0.0	−0.000217	0.0
1	3	0.004335	0.0	0.0	0.0	0.0	0.000080	0.0	0.0
1	3	−0.049589	0.0	0.0	0.0	0.0	0.000486	0.0	0.0
1	3	0.183297	0.0	0.0	0.0	0.0	−0.000313	0.0	0.0
1	3	−0.004348	0.0	0.0	0.0	0.0	−0.001735	0.0	0.0
2	0	0.003785	0.0	0.0	0.0	0.0	0.000002	0.0	0.0
2	0	0.053604	0.0	0.0	0.0	0.0	0.000010	0.0	0.0
2	0	0.304583	0.0	0.0	0.0	0.0	0.000601	0.0	0.0
2	0	0.219998	0.0	0.0	0.0	0.0	0.005434	0.0	0.0
2	1	0.0	0.0	0.004280	0.0	0.0	0.0	0.0	0.000096
2	1	0.0	0.0	−0.037693	0.0	0.0	0.0	0.0	0.000374
2	1	0.0	0.0	0.125400	0.0	0.0	0.0	0.0	0.001259
2	1	0.0	0.0	−0.057528	0.0	0.0	0.0	0.0	0.000217
2	2	0.0	0.0	0.0	0.004280	0.0	0.0	−0.000096	0.0
2	2	0.0	0.0	0.0	−0.037693	0.0	0.0	−0.000374	0.0
2	2	0.0	0.0	0.0	0.125400	0.0	0.0	−0.001259	0.0
2	2	0.0	0.0	0.0	−0.057528	0.0	0.0	−0.000217	0.0
2	3	−0.004335	0.0	0.0	0.0	0.0	0.000080	0.0	0.0
2	3	0.049589	0.0	0.0	0.0	0.0	0.000486	0.0	0.0
2	3	−0.183297	0.0	0.0	0.0	0.0	−0.000313	0.0	0.0
2	3	0.004348	0.0	0.0	0.0	0.0	−0.001735	0.0	0.0

(b)

Atom	Type	Component 1 Real	Component 1 Imaginary	Component 2 Real	Component 2 Imaginary	Component 3 Real	Component 3 Imaginary	Component 4 Real	Component 4 Imaginary
1	0	0.004185	0.0	0.0	0.0	0.0	−0.000003	0.0	0.0
1	0	0.052098	0.0	0.0	0.0	0.0	−0.000070	0.0	0.0

TABLE XII. (Continued).

Atom	Type	Component 1		Component 2		Component 3		Component 4	
		Real	Imaginary	Real	Imaginary	Real	Imaginary	Real	Imaginary
1	0	0.360 531	0.0	0.0	0.0	0.0	-0.000 210	0.0	0.0
1	0	0.210 670	0.0	0.0	0.0	0.0	-0.001 013	0.0	0.0
1	1	0.0	0.0	0.001 552	0.0	0.0	0.0	0.0	0.000 100
1	1	0.0	0.0	-0.004 875	0.0	0.0	0.0	0.0	0.000 404
1	1	0.0	0.0	0.010 410	0.0	0.0	0.0	0.0	0.001 080
1	1	0.0	0.0	-0.025 068	0.0	0.0	0.0	0.0	0.000 339
1	2	0.0	0.0	0.0	0.001 552	0.0	0.0	-0.000 100	0.0
1	2	0.0	0.0	0.0	-0.004 875	0.0	0.0	-0.000 404	0.0
1	2	0.0	0.0	0.0	0.010 410	0.0	0.0	-0.001 080	0.0
1	2	0.0	0.0	0.0	-0.025 068	0.0	0.0	-0.000 339	0.0
1	3	-0.001 972	0.0	0.0	0.0	0.0	0.000 096	0.0	0.0
1	3	0.006 358	0.0	0.0	0.0	0.0	0.000 418	0.0	0.0
1	3	0.052 506	0.0	0.0	0.0	0.0	0.001 097	0.0	0.0
1	3	0.050 493	0.0	0.0	0.0	0.0	-0.000 172	0.0	0.0
1	11	0.0	0.0	0.0	0.0	0.0	0.0	-0.000 141	0.000 141
1	12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	13	0.0	0.0	0.012 475	0.012 475	0.0	0.0	0.0	0.0
1	14	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	15	-0.015 622	0.0	0.0	0.0	0.0	0.000 250	0.0	0.0
2	0	0.004 185	0.0	0.0	0.0	0.0	0.000 003	0.0	0.0
2	0	0.052 098	0.0	0.0	0.0	0.0	0.000 070	0.0	0.0
2	0	0.360 531	0.0	0.0	0.0	0.0	0.000 210	0.0	0.0
2	0	0.210 670	0.0	0.0	0.0	0.0	0.001 013	0.0	0.0
2	1	0.0	0.0	-0.001 552	0.0	0.0	0.0	0.0	0.000 100
2	1	0.0	0.0	0.004 875	0.0	0.0	0.0	0.0	0.000 404
2	1	0.0	0.0	-0.010 410	0.0	0.0	0.0	0.0	0.001 080
2	1	0.0	0.0	0.025 068	0.0	0.0	0.0	0.0	0.000 339
2	2	0.0	0.0	0.0	-0.001 552	0.0	0.0	-0.000 100	0.0
2	2	0.0	0.0	0.0	0.004 875	0.0	0.0	-0.000 404	0.0
2	2	0.0	0.0	0.0	-0.010 410	0.0	0.0	-0.001 080	0.0
2	2	0.0	0.0	0.0	0.025 068	0.0	0.0	-0.000 339	0.0
2	3	0.001 972	0.0	0.0	0.0	0.0	0.000 096	0.0	0.0
2	3	-0.006 358	0.0	0.0	0.0	0.0	0.000 418	0.0	0.0
2	3	-0.052 506	0.0	0.0	0.0	0.0	0.001 097	0.0	0.0
2	3	-0.050 493	0.0	0.0	0.0	0.0	-0.000 172	0.0	0.0
2	11	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	13	0.0	0.0	0.012 475	0.012 475	0.0	0.0	0.0	0.0
2	14	0.0	0.0	0.0	0.0	0.0	0.0	0.000 141	-0.000 141
2	15	-0.015 622	0.0	0.0	0.0	0.0	-0.000 250	0.0	0.0

TABLE XIII. Ω eigenspinor for the ground state of H_2^+ in a Gaussian-lobe basis set of (a) s and p functions and (b) s, p, and d functions. Type designations, see Table XII.

(a)

Atom	Type	Component 1 Real	Component 1 Imaginary	Component 2 Real	Component 2 Imaginary	Component 3 Real	Component 3 Imaginary	Component 4 Real	Component 4 Imaginary
1	0	0.004191	0.0	0.0	0.0	0.0	−0.000004	0.0	0.0
1	0	0.052568	0.0	0.0	0.0	0.0	−0.000036	0.0	0.0
1	0	0.356041	0.0	0.0	0.0	0.0	−0.000414	0.0	0.0
1	0	0.218546	0.0	0.0	0.0	0.0	−0.001440	0.0	0.0
1	1	0.0	0.0	0.000000	0.0	0.0		0.0	0.000096
1	1	0.0	0.0	0.000001	0.0	0.0		0.0	0.000401
1	1	0.0	0.0	0.000002	0.0	0.0		0.0	0.001127
1	1	0.0	0.0	0.000000	0.0	0.0		0.0	0.000333
1	2	0.0	0.0	0.0	0.000000	0.0		−0.000096	0.0
1	2	0.0	0.0	0.0	0.000001	0.0		−0.000401	0.0
1	2	0.0	0.0	0.0	0.000002	0.0		−0.001127	0.0
1	2	0.0	0.0	0.0	0.000000	0.0		−0.000333	0.0
1	3	0.000037	0.0	0.0	0.0	0.0	0.000095	0.0	0.0
1	3	0.002545	0.0	0.0	0.0	0.0	0.000414	0.0	0.0
1	3	0.047077	0.0	0.0	0.0	0.0	0.000778	0.0	0.0
1	3	0.042400	0.0	0.0	0.0	0.0	−0.000281	0.0	0.0
2	0	0.004191	0.0	0.0	0.0	0.0	0.000004	0.0	0.0
2	0	0.052568	0.0	0.0	0.0	0.0	0.000036	0.0	0.0
2	0	0.356041	0.0	0.0	0.0	0.0	0.000414	0.0	0.0
2	0	0.218546	0.0	0.0	0.0	0.0	0.001440	0.0	0.0
2	1	0.0	0.0	−0.000000	0.0	0.0		0.0	0.000096
2	1	0.0	0.0	−0.000001	0.0	0.0		0.0	0.000401
2	1	0.0	0.0	−0.000002	0.0	0.0		0.0	0.001127
2	1	0.0	0.0	−0.000000	0.0	0.0		0.0	0.000333
2	2	0.0	0.0	0.0	−0.000000	0.0		−0.000096	0.0
2	2	0.0	0.0	0.0	−0.000001	0.0		−0.000401	0.0
2	2	0.0	0.0	0.0	−0.000002	0.0		−0.001127	0.0
2	2	0.0	0.0	0.0	−0.000000	0.0		−0.000333	0.0
2	3	−0.000037	0.0	0.0	0.0	0.0	0.000095	0.0	0.0
2	3	−0.002545	0.0	0.0	0.0	0.0	0.000414	0.0	0.0
2	3	−0.047077	0.0	0.0	0.0	0.0	0.000778	0.0	0.0
2	3	−0.042400	0.0	0.0	0.0	0.0	−0.000281	0.0	0.0

(b)

Atom	Type	Component 1 Real	Component 1 Imaginary	Component 2 Real	Component 2 Imaginary	Component 3 Real	Component 3 Imaginary	Component 4 Real	Component 4 Imaginary
1	0	0.004189	0.0	0.0	0.0	0.0	−0.000003	0.0	0.0
1	0	0.052625	0.0	0.0	0.0	0.0	−0.000055	0.0	0.0
1	0	0.355163	0.0	0.0	0.0	0.0	−0.000328	0.0	0.0
1	0	0.218826	0.0	0.0	0.0	0.0	−0.000992	0.0	0.0

TABLE XIII. (Continued).

Atom	Type	Component 1		Component 2		Component 3		Component 4	
		Real	Imaginary	Real	Imaginary	Real	Imaginary	Real	Imaginary
1	1	0.0	0.0	0.000000	0.0	0.0	0.0	0.0	0.000083
1	1	0.0	0.0	0.000001	0.0	0.0	0.0	0.0	0.000420
1	1	0.0	0.0	0.000001	0.0	0.0	0.0	0.0	0.001071
1	1	0.0	0.0	0.000000	0.0	0.0	0.0	0.0	0.000353
1	2	0.0	0.0	0.0	0.000000	0.0	0.0	-0.000083	0.0
1	2	0.0	0.0	0.0	0.000001	0.0	0.0	-0.000420	0.0
1	2	0.0	0.0	0.0	0.000001	0.0	0.0	-0.001071	0.0
1	2	0.0	0.0	0.0	0.000000	0.0	0.0	-0.000353	0.0
1	3	0.000037	0.0	0.0	0.0	0.0	0.000083	0.0	0.0
1	3	0.002533	0.0	0.0	0.0	0.0	0.000424	0.0	0.0
1	3	0.046685	0.0	0.0	0.0	0.0	0.000889	0.0	0.0
1	3	0.043289	0.0	0.0	0.0	0.0	-0.000102	0.0	0.0
1	11	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.000124
1	13	0.0	0.0	0.000000	0.0	0.0	0.0	-0.000124	0.0
1	14	0.0	0.0	0.0	0.000000	0.0	0.0	0.0	0.0
1	15	0.001488	0.0	0.0	0.0	0.0	0.000121	0.0	0.0
2	0	0.004189	0.0	0.0	0.0	0.0	0.000003	0.0	0.0
2	0	0.052625	0.0	0.0	0.0	0.0	0.000055	0.0	0.0
2	0	0.355163	0.0	0.0	0.0	0.0	0.000328	0.0	0.0
2	0	0.218826	0.0	0.0	0.0	0.0	0.000992	0.0	0.0
2	1	0.0	0.0	-0.000000	0.0	0.0	0.0	0.0	0.000083
2	1	0.0	0.0	-0.000001	0.0	0.0	0.0	0.0	0.000420
2	1	0.0	0.0	-0.000001	0.0	0.0	0.0	0.0	0.001071
2	1	0.0	0.0	-0.000000	0.0	0.0	0.0	0.0	0.000353
2	2	0.0	0.0	0.0	-0.000000	0.0	0.000083	-0.000083	0.0
2	2	0.0	0.0	0.0	-0.000001	0.0	0.000424	-0.000420	0.0
2	2	0.0	0.0	0.0	-0.000001	0.0	0.000889	-0.001071	0.0
2	2	0.0	0.0	0.0	-0.000000	0.0	-0.000102	-0.000353	0.0
2	3	-0.000037	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	3	-0.002533	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	3	-0.046685	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	3	-0.043289	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	11	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	13	0.0	0.0	0.000000	0.0	0.0	0.0	0.000124	0.0
2	14	0.000124	0.0	0.0	0.000000	0.0	0.0	0.0	-0.000124
2	15	0.001488	0.0	0.0	0.0	0.0	-0.000121	0.0	0.0

have π-type contributions. On comparison with Table XI (b), the spinor can be identified as a linear combination of a $s\sigma_{g1/2}$ and a $p\sigma_{g1/2}$ spinor. The alternating signs in the $p\sigma_{g1/2}$ contributions indicate that the latter stem from a virtual spinor, which should have an energy much higher than the ground-state energy.

Table XIII (a) shows the corresponding spinor calculated with Ω. The spurious π contributions in the upper components are negligible. However, one can observe a polarization along the (internuclear) z axis by means of the σ-type basis functions. This is in agreement with the fact that only the projection of $\vec{j} = \vec{l} + \vec{s}$ onto the internuclear axis provides a good quantum number for classifying molecular spinors in linear molecules.

Inclusion of d-type functions in the basis set reduces the π-type contributions to the Dirac eigenspinor by an order of magnitude [Table XII (b)]. The main effect of the additional d functions is probably to improve the representation of the virtual spinor. Its energy gets more reasonable and mixing with the ground-state spinor is reduced. Apart from further polarization, the d functions have no significant effect on the Ω eigenspinor [Table XIII (b)].

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