in accord with the theoretical estimate given above and elsewhere.[8] The strong line in Fig. 2(c) at 1300 keV corresponds well to the estimate given above for the $h_{9/2}$ proton and we would tentatively make that identification. More systematic data will be needed to make firm assignments throughout the high-spin regions, but the observation of specific alignment frequencies in an unresolved spectrum represents a significant step in understanding nuclei at the highest angular momentum.

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New Representation of the $\vec{\alpha}\cdot\vec{p}$ Operator in the Solution of Dirac-Type Equations by the Linear-Expansion Method

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The solution of Dirac-type equations by the linear expansion technique suffers from variational instability due to difficulties in obtaining accurate matrix representations of the $\vec{\alpha}\cdot\vec{p}$ operator in conventional basis sets. A new matrix representation of $\vec{\alpha}\cdot\vec{p}$ is proposed which resolves the problem. The method has been successfully applied in numerical calculations.

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Fully relativistic quantum mechanical electronic structure calculations are usually based on Dirac-Coulomb-type Hamiltonians,[1]

$$H=\sum_{i}^{n} h_{\mathrm{D}}(i)+\sum_{i>j}^{n} g(i,j)$$

with

$$h_{\mathrm{D}}=c^2\beta' m+c\vec{\alpha}\cdot\vec{p}+V.$$

For atomic systems, as a result of central field symmetry, quite close approximations to the eigenvalue equation $H\psi=E\psi$ can be obtained by one-dimensional numerical integration, for instance within the independent-particle model.[2] For molecular multicenter systems one is forced for computational reasons to approximate the wave function by expanding it linearly into some finite basis set. However, in the relativistic case variational instability arises which does not occur in the expansion of the Schrödinger operator. Since the Dirac one-electron Hamiltonian h_D is not bounded from below, the calculated energy may be higher or lower than the exact one. Furthermore, calculations for atoms[3] and particularly for molecules[4] have shown that the energy depends sensitively on small changes in the basis set. Consequently, it is very difficult to obtain any reliable relativistic energy corrections. This variational instability has already been discussed[4c,5] and methods to cure the so-called "finite basis set disease"[5b] have been proposed.[4b,4c,5a,6,7] However, they either require involved computation[5a,6] or have been subject to criticism.[5b] Here a simple alternative is proposed which overcomes these difficulties. Its efficiency is demonstrated by test calculations on H and H_2^+.

The problems with finite-basis approximations of the one-particle Dirac equation

$$(V+c\vec{\alpha}\cdot\vec{p}+c^2\beta' m)\psi=E\psi \tag{1}$$

arise[5] mainly from the representation of the relativisitc kinetic energy operator $\vec{\alpha}\cdot\vec{p}$. Two arguments lead us to introduce an improved type of representation.

First, if the Dirac equation is derived from the Klein-Gordon equation by linearization of the kinetic energy, the operator $\vec{\alpha}\cdot\vec{p}$ is defined to fulfill, among others, the relation

$$(\vec{\alpha}\cdot\vec{p})(\vec{\alpha}\cdot\vec{p})^\dagger=\vec{p}^{\,2}, \tag{2}$$

with $\vec{\alpha}\cdot\vec{p}=(\vec{\alpha}\cdot\vec{p})^\dagger$. Now, for finite (orthonormal) basis sets $\{k\}$ the resolution of the identity holds only approximately: $\sum_k |k\rangle\langle k|\neq 1$, so that

$$\begin{aligned}\langle i|\vec{p}^{\,2}|j\rangle &= \langle i|(\vec{\alpha}\cdot\vec{p})(\vec{\alpha}\cdot\vec{p})|j\rangle\\ &= \langle i|(\vec{\alpha}\cdot\vec{p})\cdot 1\cdot(\vec{\alpha}\cdot\vec{p})|j\rangle\\ &\neq \textstyle\sum_k \langle i|\vec{\alpha}\cdot\vec{p}|k\rangle\langle k|\vec{\alpha}\cdot\vec{p}|j\rangle.\end{aligned}$$

Hence, denoting matrix representations by square brackets, we have

$$[\vec{\alpha}\cdot\vec{p}][\vec{\alpha}\cdot\vec{p}]^\dagger\neq[\vec{p}^{\,2}], \tag{2a}$$

contrary to Eq. (2). We introduce a modified representation $[\vec{\alpha}\cdot\vec{p}]_{\rm mod}$ which is forced to fulfill the same relation as the operator $(\vec{\alpha}\cdot\vec{p})$,

$$[\vec{\alpha}\cdot\vec{p}]_{\rm mod}[\vec{\alpha}\cdot\vec{p}]_{\rm mod}^\dagger=[\vec{p}^{\,2}]. \tag{2b}$$

Second, in the nonrelativistic limit $c\to\infty$, one obtains from Eq. (1) for the so-called positive-energy solutions with energy E_+

$$\{V+(\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{p})/2m\}\psi_+=E_+\psi_+, \tag{3}$$

where ψ_+ stands for the upper two components of the four-component spinor

$$\psi=\begin{pmatrix}\psi_+\\ \psi_-\end{pmatrix}.$$

Since for the two-by-two operators,

$$(\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{p})^\dagger=\vec{p}^{\,2} \tag{4}$$

is valid, Eq. (3) is identical with the Schrödinger equation. Again, the operator equation no longer holds for finite basis sets, where in general

$$[\vec{\sigma}\cdot\vec{p}][\vec{\sigma}\cdot\vec{p}]\neq[\vec{p}^{\,2}]. \tag{4a}$$

As a consequence of Eq. (4a) the finite-basis-set representation of the Dirac equation fails to give the proper nonrelativistic limit. Furthermore, since

$$\mathrm{tr}([\vec{\sigma}\cdot\vec{p}][\vec{\sigma}\cdot\vec{p}]^\dagger)\leq\mathrm{tr}[\vec{p}^{\,2}],$$

the resulting kinetic and consequently total energies[4,5a] are too low. This imbalance is removed and the proper nonrelativistic limit is reestablished by the introduction of the modified matrix representation

$$[\vec{\sigma}\cdot\vec{p}]_{\rm mod}[\vec{\sigma}\cdot\vec{p}]_{\rm mod}^\dagger=[\vec{p}^{\,2}], \tag{4b}$$

which is consistent with Eq. (2b) if

$$[\vec{\alpha}\cdot\vec{p}]_{\rm mod}=\begin{pmatrix}[0] & [\vec{\sigma}\cdot\vec{p}]_{\rm mod}\\ [\vec{\sigma}\cdot\vec{p}]_{\rm mod}^\dagger & [0]\end{pmatrix}.$$

It is an essential feature of our approach that as a result of condition (4b) for *any basis* the relativistic energy converges to the nonrelativistic one for $c\to\infty$, whereas in the quasinonrelativistic approach[4b,4c] this limit is obtained only for complete basis sets.

Equations (2b) or (4b) define the modified representation only up to a unitary matrix. As an additional condition to fix $[\vec{\sigma}\cdot\vec{p}]_{\rm mod}$ we impose that the Euclidean norm of the relative difference[8] of $[\vec{\sigma}\cdot\vec{p}]_{\rm mod}$ and $[\vec{\sigma}\cdot\vec{p}]$ should be as small as possi-

TABLE I. $1S_{1/2}$ energy and relativistic energy correction of the H atom from different basis sets (10^{-6} a.u.).

primitive/contracted Gaussians of s,p-type	deviation of calc. energy from exact value			relativistic correction $\Delta E = E_{nrel} - E_{rel}$	
	$[h_D]$	$[h_D]_{mod}$	$[h_{Schrödinger}]$	with $[h_D]$	with $[h_D]_{mod}$
2,2	-43 980.037	+14 932.508	+14 931.038	58 917.732	5.187
3,3	-11 362.633	3 285.848	3 285.219	14 654.509	6.028
4,4	- 2 319.510	812.478	812.046	3 138.213	6.225
5,5	- 513.740	222.069	221.970	742.367	6.558
6,6	- 161.260	66.196	66.122	234.039	6.583
7,7	- 77.249	21.194	21.183	105.089	6.646
8,8	- 39.727	7.228	7.220	53.604	6.649
12,14/7,7	- 2.986	0.160	0.161	9.804	6.657
14,16/7,7	- 2.747	0.028	0.029	9.433	6.657
limit	(-500 006.657)		(-500 000.000)	6.657	

TABLE II. Ground-state energy and relativistic energy correction of H_2^+ ($R = 2a_0$) calculated with different basis sets (10^{-6} a.u.).

primitive/contracted Gaussians of s,p,d,f-type	deviation of calc. energy from exact value			relativistic correction $\Delta E = E_{nrel} - E_{rel}$	
	$[h_D]$	$[h_D]_{mod}$	$[h_{Schrödinger}]$	with $[h_D]$	with $[h_D]_{mod}$
s,p-basis					
2,2/2,2	-60 698.7	27 433.7	+27 433.4	88 139.5	7.02
3,3/3,3	+ 5 853.5	5 846.4	5 845.2	- 0.9	6.17
4,4/3,3	-57 773.2	1 863.8	1 863.4	59 644.0	6.97
5,5/4,4	-16 945.1	657.7	657.2	17 609.7	6.97
7,7/5,5	+26 686.0	336.8	336.5	-26 342.1	7.06
12,14/7,7	-16 428.4	223.4	223.3	16 659.1	7.27
s,p,d-basis					
4,4,1/4,4,1	- 4 390.3	1 506.7	1 506.6	5 904.3	7.23
5,5,1/4,4,1	- 1 447.3	495.4	495.3	1 950.0	7.32
12,14,1/7,7,1	- 485.9	13.1	13.1	506.4	7.41
12,14,2/7,7,2	+ 1 054.5	5.1	5.1	- 1 042.1	7.39
12,14,3/7,7,3	- 170.3	4.2	4.2	181.9	7.36
s,p,d,f-basis					
12,14,3,1/7,7,3,1	- 1 105.3	1.7	1.7	1 114.4	7.36
limit[9]	(-1 102 641.6)		(-1 102 634.2)	7.38	

ble:

$$||[\vec{\sigma}\cdot\vec{p}\,]^{-1}([\vec{\sigma}\cdot\vec{p}\,]_{\mathrm{mod}}-[\vec{\sigma}\cdot\vec{p}\,])|| \rightarrow \text{minimum}. \tag{5}$$

Conditions (4b) and (5) result in

$$[\vec{\sigma}\cdot\vec{p}\,]_{\mathrm{mod}} =[\vec{\sigma}\cdot\vec{p}\,]([\vec{\sigma}\cdot\vec{p}\,]^{-1}[\vec{p}^{\,2}][\vec{\sigma}\cdot\vec{p}\,]^{-1})^{1/2}. \tag{6}$$

For complete basis sets $[\vec{\sigma}\cdot\vec{p}\,]_{\mathrm{mod}}$ reduces to the exact matrix representation $[\vec{\sigma}\cdot\vec{p}\,]$ as required. Zero eigenvalues of $[\vec{\sigma}\cdot\vec{p}\,]$ can be avoided for bound states by appropriate choice of the basis so that $[\vec{\sigma}\cdot\vec{p}\,]^{-1}$ exists.

In order to demonstrate the efficiency of the proposed modification we performed calculations on two one-electron systems, H and H_2^+. So-called scalar basis sets[4c] of Gaussian lobe type have been used. The exponents of the s and p Gaussians were determined by a least-squares fit to the exact hydrogen $1S_{1/2}$ solution, and of the d and f Gaussians by approximate minimization of the nonrelativistic energy. We have taken $c = 137.036\,02$ a.u.

The ground-state energy E and the relativistic energy correction $\Delta E = E_{\mathrm{nrel}} - E_{\mathrm{rel}}$ of the hydrogen atom are given in Table I for various basis sets. The convergence behaviors of the relativistic E values from the improved representation $[h_{\mathrm{D}}]_{\mathrm{mod}}$ and of the nonrelativistic E values show a parallel trend. When the basis size is increased, the energies derived from $[h_{\mathrm{D}}]_{\mathrm{mod}}$ converge from above as in the nonrelativistic case, whereas the energies from the conventional $[h_{\mathrm{D}}]$ converge from below in this representative example. Furthermore, the convergence is much slower for $[h_{\mathrm{D}}]$. This holds in particular for the ΔE values. For the largest basis the error of the nonrelativistic energy is smaller by orders of magnitude than the relativistic energy correction. Nevertheless ΔE from the conventional $[h_{\mathrm{D}}]$ is still in error by about 42%.

Similar results are obtained for the H_2^+ molecule (Table II). Although the relativistic energy correction is quite small,[9] even with very limited basis sets, reasonable values are obtained from $[h_{\mathrm{D}}]_{\mathrm{mod}}$. In contrast, the energies from $[h_{\mathrm{D}}]$ oscillate so erratically that no limiting value can be deduced. Such a behavior of $[h_{\mathrm{D}}]$ is typical for the multicenter case.

Since the difficulties in finite-basis-set approximations of the Dirac equation arise from the one-electron $\vec{\alpha}\cdot\vec{p}$ operator, similar improved results may be anticipated if the two-electron interaction is taken into account. This is indeed confirmed by actual calculations. Corresponding results for many-electron systems and details of the method will be published soon.

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