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Dirac-Fock calculations for the ground states of some small molecules

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We present basis-set Dirac-Fock calculations of the ground states of the H_2, HF, HCl, H_2O, NH_3, and CH_4 molecules. Molecular orbitals are constructed by linearly combining four-component spherical spinors centered at the nuclei; the radial dependence of the large component is $r^n e^{-\xi r^2}$, where n is a nonnegative integer determined by the angular quantum numbers, and $\xi \in a, ab, ab^2, \ldots$, where $a > 0$ and $b > 1$ are real numbers; the small component is generated from the large component using the "strict kinetic balance" prescription. Our estimates of the ground-state energies of these molecules decrease monotonically as the size of the basis sets used is enlarged. The nonrelativistic (essentially basis-set Hartree-Fock) limits of our calculations are obtained by increasing the speed of light by a few orders of magnitude over its physical value; we are thus able to estimate relativistic corrections in an unambiguous way within the context of our molecular models.

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I. INTRODUCTION

"Fully relativistic" numerical calculations based on the Dirac kinetic-energy Hamiltonian and four-component spinor orbitals have been employed with notable success for several decades in theoretical studies of atomic structure [1]. Although Kim [2] generalized the expansion method of Roothaan [3] to fully relativistic calculations for atoms almost 30 years ago, early difficulties [4] prevented the application of the method with widespread success until relatively recently. One way of circumventing difficulties in practical calculations has been to impose the condition of "kinetic balance" [5–7] between the large- and small-component basis functions.

Gaussian-type atomic orbitals are a felicitous choice for the construction of models of polyatomic molecules because of the relative ease with which many-center two-electron integrals can be computed. Kinetically balanced Gaussian basis sets have been employed to calculate the ground-state energies of a number of atoms and ions [8–12]. Although the stability and convergence properties of this procedure have not been established in a rigorous way, numerical evidence suggests that practical calculations are stable and the accuracy achieved in these calculations is comparable with that of their numerical counterparts [13]; the search for alternative basis sets, alternative variational principles, or both continues, essentially unabated [14]. Relativistic atomic-structure calculations using Gaussian basis functions constitute the first step in the construction of the relativistic generalization of the linear combination of atomic orbitals–molecular orbitals (LCAO-MO) method [15].

The first Dirac-Fock basis-set calculations for polyatomic molecules extended the kinetic-balance condition to standard Cartesian Gaussian-type functions in a scalar basis [16]. More recently, a prescription for constructing relativistic basis spinors for molecules based on atom-centered spinor spherical-harmonic Gaussian-type functions with "strict" kinetic balance [6] has been proposed [17–19]. Several calculations employing spinor spherical-harmonic Gaussian-type functions have appeared in the recent literature [20,21]. Contracted Gaussian-type functions have been used to reduce the computational effort in most of these calculations, which remain orders of magnitude more demanding of processor effort and storage than typical relativistic atomic-structure calculations.

In the present work we employ uncontracted spherical-spinor Gaussian-type atomic orbitals, which satisfy the condition of strict kinetic balance. Our formalism [19] is a straightforward generalization of kinetically balanced spherical-spinor Gaussian-type atomic orbitals to the LCAO-MO method. The exponents for all symmetries are members of the same geometric sequence [22,23,9,19] and, since the basis functions are left uncontracted, the augmentation of the basis set to diminish truncation error is particularly straightforward. Some details of our formalism are presented in Sec. II. We have studied a number of closed-shell molecular systems; our results are given in Sec. III; these results provide numerical evidence for the upper-bound properties of our estimates of the ground-state energy. A summary of our work is given in Sec. IV, the Conclusion.

II. DIRAC-FOCK PROCEDURE FOR MOLECULAR SYSTEMS

A detailed presentation of the theoretical and computational aspects of our work will appear elsewhere; here we restrict ourselves to a brief overview. We essentially adopt the procedure described in [19], except for a choice of phases to maintain consistency with earlier atomic-structure calculations [10,11].

An approximate relativistic Hamiltonian—the Dirac-Coulomb Hamiltonian—for a system of N^e electrons and N^n stationary nuclei may be readily constructed by combining Dirac kinetic-energy operators,[1] for each constituent electron

$$H^D = c\boldsymbol{\alpha}\cdot\mathbf{p} + (\beta-1)c^2 , \tag{2.1}$$

and Coulomb interaction operators

$$H^C = \frac{q_1 q_2}{|\mathbf{r}_1-\mathbf{r}_2|} , \tag{2.2}$$

for each pair of point particles. Thus

$$H^{[N^e]} = \sum_{i=1}^{N^e} H_i^D + \sum_{i=1}^{N^e-1}\sum_{j=i+1}^{N^e} \frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_{i=1}^{N^e}\sum_{j=1}^{N^n} \frac{Z_j}{|\mathbf{r}_i-\mathbf{C}_j|} . \tag{2.3}$$

Here we have neglected the motional energy of the nuclei. This approximation, due to Born and Oppenheimer [24], is a common starting point for molecule electronic-structure calculations. The interaction between the nuclei contributes an energy of

$$\sum_{i=1}^{N^n-1}\sum_{j=i+1}^{N^n} \frac{Z_i Z_j}{|\mathbf{C}_i-\mathbf{C}_j|} . \tag{2.4}$$

A wave function for an electron interacting with a set of nuclei may be constructed by combining "basis functions" centered on each nucleus. The choice of the latter functions is a compromise between physically reasonable behavior and computational convenience. In our case the functions at each center $\mathbf{C}$ are four-component spinors

$$X\psi(\mathbf{r}) = \begin{bmatrix} X^P\chi^P(\mathbf{r}) \\ iX^Q\chi^Q(\mathbf{r}) \end{bmatrix} , \tag{2.5}$$

where X and $X^{T\,(=P,Q)}$ are complex numbers and $\chi^T(\mathbf{r})$ is a two-component function of the coordinates with respect to the center. The basis functions (2.5) are approximate atomic wave functions; this choice is drawn from the physically reasonable assumption that the largest contribution to the energy due to the interaction of an electron with a given nucleus arises from the electronic density closest to the nucleus and in this region the form of the wave function resembles that in a "free" atomic system. The function (2.5) is an eigenstate of the operator of total angular momentum $\mathbf{j}=\mathbf{l}+\mathbf{s}$ and of the relativistic operator of inversion $P=\beta\pi$, where π is the familiar operator of inversion

$$\begin{aligned} &\mathbf{j}^2 X\psi(\mathbf{r}) = j(j+1)X\psi(\mathbf{r}) , \quad j=\tfrac{1}{2},\tfrac{3}{2},\tfrac{5}{2},\ldots \\ &j_z X\psi(\mathbf{r}) = mX\psi(\mathbf{r}) , \quad m=-j,-j+1,\ldots,j-1,j \\ &PX\psi(\mathbf{r}) = (-1)^l X\psi(\mathbf{r}) , \quad l=j\pm\tfrac{1}{2} . \end{aligned} \tag{2.6}$$

The eigenstate of operators that commute with the one-electron Hamiltonian of an atom (this Hamiltonian includes the electron-nuclear interaction term) are called atomic orbitals (AOs). A molecular orbital (MO), obtained by linearly combining AOs, yields the LCAO-MO expansion

$$\phi_I(\mathbf{r}) = \sum_p X_{Ip}\psi_p(\mathbf{r}_p) . \tag{2.7}$$

In practical applications, the summation is over a finite number of terms; the equality in (2.7) must then be replaced by an approximate equality; the resulting expansion will be referred to as the LCAO-MO approximation. The coordinate $\mathbf{r}_p=\mathbf{r}-\mathbf{C}_p$ is the position vector relative to the center of the AO with index p. The large-component basis function $\chi_p^P(\mathbf{r}_p)$ in (2.5) is taken to be of the form

$$\chi_p^P(\mathbf{r}_p) = N_{\kappa_p}^P(\xi_p) r_p^{n_{\kappa_p}} e^{-\xi_p r_p^2} \frac{1}{r_p} \Omega_{\kappa_p m_p}(\hat{\mathbf{r}}_p) ; \tag{2.8}$$

here $N_{\kappa_p}^P(\xi_p)$ is a normalization constant defined so that the integral over all space of (2.8) is unity,

$$\kappa = -(2j+1)(j-l) \tag{2.9}$$

is the relativistic angular quantum number, and $\Omega_{\kappa m}(\hat{\mathbf{r}}) = \Omega_{ljm}(\hat{\mathbf{r}})$ is a two-component spinor spherical harmonic

$$\Omega_{ljm}(\hat{\mathbf{r}}) = \sum_{\sigma=\pm\frac{1}{2}} C_{l,m-\sigma;1/2,\sigma}^{jm} Y_{l,m-\sigma}(\hat{\mathbf{r}})\chi_\sigma . \tag{2.10}$$

In the above formula $C_{a\alpha;b\beta}^{c\gamma}$ is a Clebsch-Gordan coefficient, $Y_{l,m}(\hat{\mathbf{r}})$ is a spherical harmonic, and χ_σ is a two-component spin function. In Eq. (2.8),

$$n_\kappa = \begin{cases} -\kappa & \text{if } \kappa<0 \\ \kappa+1 & \text{if } \kappa>0 . \end{cases} \tag{2.11}$$

One small-component function $\chi_p^Q(\mathbf{r}_p)$ in (2.5)

$$\chi_p^Q(\mathbf{r}_p) = N_{\kappa_p}^Q(\xi_p) N_{\kappa_p}^P(\xi_p) \times [(n_{\kappa_p}+\kappa_p) r_p^{n_{\kappa_p}-1} - 2\xi_p r_p^{n_{\kappa_p}+1}] \times e^{-\xi_p r_p^2} \frac{1}{r_p} \Omega_{-\kappa_p m_p}(\hat{\mathbf{r}}_p) \tag{2.12}$$

corresponds to *each* large-component function (2.8) in (2.5). The additional normalization factor $N_{\kappa_p}^Q(\xi_p)$ ensures that the integral over all space of $\chi_p^Q(\mathbf{r}_p)$ is unity.

The functions (2.8) and (2.12) satisfy the condition of "strict kinetic balance" [6]

$$\chi_p^Q(\mathbf{r}_p) \propto (\boldsymbol{\sigma}\cdot\mathbf{p})\chi_p^P(\mathbf{r}_p) , \tag{2.13}$$

where $\boldsymbol{\sigma}$ are the Pauli spin matrices. Application of (2.13) to a large- component function with $1s_{1/2}$ symmetry (our prototype $\kappa<0$ function) generates *one* function with $2p_{1/2}$ symmetry; however, application of (2.13) to a large-component function with $2p_{1/2}$ symmetry ($\kappa>0$)

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[1] We employ Hartree atomic units throughout, unless explicitly stated otherwise. In this system of units, $\hbar=m^e=e=1$, where $\hbar=h/2\pi$ and h is the Planck constant, m^e is the mass of the electron, and e is the charge on the proton. It follows that $\alpha=1/c$, where $\alpha\approx1/137$ is the fine-structure constant and c is the vacuum speed of light.

generates a *fixed linear combination of two functions* with $1s_{1/2}$ and $3s_{1/2}$ symmetry, respectively [Eq. (2.12)]. The latter combination is in one-to-one correspondence with the $2p_{1/2}$ large-component function. In "extended" kinetic balance, the $1s_{1/2}$ and $3s_{1/2}$ functions are independently varied [25].

A single Slater determinant of order N^e of molecular orbitals is an approximate wave function for an N^e-electron closed-shell molecular system. In the Dirac-Fock method, an energy functional is constructed from the expectation value of the Hamiltonian (2.3) with respect to such an approximate wave function and is augmented with terms that ensure the orthonormality of the MOs (2.5). The extremum of this functional with respect to variations in the coefficients X^T is obtained from the solution of the Dirac-Fock-Roothaan equation

$$\mathbf{F}\mathbf{X}_I=\epsilon_I\mathbf{S}\mathbf{X}_I \; . \tag{2.14}$$

Equation (2.14) is a matrix equation; here

$$\mathbf{F}=\begin{bmatrix} \mathbf{V}^{PP}+\mathbf{J}^{PP}-\mathbf{K}^{PP} & c\mathbf{\Pi}^{PQ}-\mathbf{K}^{PQ} \\ c\mathbf{\Pi}^{QP}-\mathbf{K}^{QP} & \mathbf{V}^{QQ}-2c^2\mathbf{S}^{QQ}+\mathbf{J}^{QQ}-\mathbf{K}^{QQ} \end{bmatrix} \tag{2.15}$$

is the relativistic Fock matrix,

$$\mathbf{S}=\begin{bmatrix} \mathbf{S}^{PP} & 0 \\ 0 & \mathbf{S}^{QQ} \end{bmatrix} , \tag{2.16}$$

is the relativistic overlap matrix, and

$$\mathbf{X}_I=\begin{bmatrix} \mathbf{X}_I^P \\ \mathbf{X}_I^Q \end{bmatrix} . \tag{2.17}$$

The various submatrices are essentially as described in Ref. [19].

The familiar nonrelativistic formalism is obtained in the limit $c\to\infty$. Correct nonrelativistic limits of relativistic molecular-structure calculations will be obtained only if the basis set has been properly selected. In the context of atomic structure, the quantum number l is a "good" quantum number in this limit; relativistic orbitals with different values of the quantum number j but the same value of the quantum number l are degenerate in the nonrelativistic limit. In LCAO-MO calculations, it is therefore necessary to choose identical basis sets for the "spin-orbit components" of each "atomic" basis set. Further, in comparing nonrelativistic limits to the results of a calculation that is nonrelativistic from the outset, care must be taken to ensure that the nonrelativistic model is compatible: in the present case, the nonrelativistic model must be based on spherical Gaussian functions.

The radial dependences of the kinetically balanced Gaussian functions (2.8) and (2.12) are partially governed by the exponents ξ_p. These are taken to be contiguous members of a geometric sequence

$$a, ab, ab^2, ab^3, \ldots \; . \tag{2.18}$$

For a given species (Z, A), the set of exponents for a symmetry with a higher j or l quantum number is a subset of the exponents for a symmetry with lower values of these quantum numbers. Such basis functions have evolved from the "even-tempered" [22] and "geometric" [23] prescriptions and have played an important role in the assessment of the reliability of relativistic atomic-structure calculations [9–11]. The basis set for all centers with atomic number Z is identical. Basis functions with all possible values of the quantum number m are generated for a given value of the quantum number j.

III. CALCULATIONS FOR POLYATOMIC MOLECULES

We have applied our method and our RELMOL computer program package to the calculation of the ground-state energies of several neutral molecular systems. In all our calculations classified as relativistic, the speed of light has been taken to be 137.035 989 5 a.u. [26]; the Bohr radius has been taken to be 0.529 177 249 Å [26]. One- and two-electron integrals of absolute magnitude less than 10^{-12} are disregarded; a self-consistent-field (SCF) calculation is considered converged when density-matrix elements from successive iterations differ by less than one part in 10^{12}. Due to the one-to-one correspondence between large- and small-component basis functions [Eqs. (2.8) and (2.12)], the generalized eigenvalue problem (2.14) is always of even order. The eigenvalue spectrum may therefore be separated exactly into a lower half and an upper half when the eigenvalues are arranged in ascending order. All eigenvalues in the lower half of the spectrum lie below $-2c^2$. All eigenvalues in the upper half lie above $-2c^2$. The eigenvectors corresponding to the lowest N^e eigenvalues in the latter half of the spectrum contribute to the density matrix; this ensures that an implicit "no-pair" formulation of relativistic electron theory is used [27].

As mentioned previously, atomic nuclei are assumed to be point sources in our calculations. "Point nuclei" are almost invariably used in nonrelativistic molecular electronic structure calculations. Models that account for nuclear extent, referred to here as "finite nuclei," are frequently, but not invariably, used in relativistic calculations. Energy differences due to different nuclear models are expected to be a few microhartrees in C and N, a few tens of microhartrees in O and F, and a few hundreds of microhartrees in Cl. In the calculations presented in Tables I–VI below, these differences are small compared with other effects that lead to the various predictions of molecular energies.

The nonrelativistic limit may be simulated in a relativistic program by increasing the speed of light from its measured value. The factor 10^4 is found to be adequate.[2]

The two-electron H_2 molecule is the first many-electron system we discuss. Our results are presented in Table I. The small discrepancies between our nonrelativistic limits and the results of Wells and Wilson [29] are

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[2] A systematic procedure for obtaining nonrelativistic limits has been described in Table III in Ref. [11]. Also see Ref. [28].

TABLE I. Total energies (in hartrees) for the ground state of the H_2 molecule. The nuclei have been assumed to be stationary point particles separated by $1.4a_0$.

	Calculation	E
$c=137.035\,989\,5$	$23s$[a]	$-1.128\,555\,704\,3$
	$23s/9p$[a]	$-1.133\,586\,187\,4$
	$23s/9p/4d$[a]	$-1.133\,642\,857\,1$
	$23s/9p/4d/2f$[a]	$-1.133\,643\,502\,3$
	$23s/9p/4d/4f$[a]	$-1.133\,643\,833\,4$
	finite element[b]	$-1.133\,643\,970\,08(1)$
$c\rightarrow 10^4c$	$23s$[a]	$-1.128\,542\,170\,3$
	$23s/9p$[a]	$-1.133\,571\,814\,4$
	$23s/9p/4d$[a]	$-1.133\,628\,459\,9$
	$23s/9p/4d/2f$[a]	$-1.133\,629\,104\,6$
	$23s/9p/4d/4f$[a]	$-1.133\,629\,435\,4$
Nonrelativistic	$23s$[c]	$-1.128\,542\,094$
	$23s/9p$[c]	$-1.133\,571\,746$
	$23s/9p/4d$[c]	$-1.133\,628\,387$
	$23s/9p/4d/2f$[c]	$-1.133\,629\,033$
	$23s/9p/4d/4f$[c]	$-1.133\,629\,363$
	finite element[b]	$-1.133\,629\,571\,7(2)$

[a] RELMOL calculation: exponents from Wells and Wilson [29].
[b] Reference [30].
[c] Reference [29].

probably due to different choices of thresholds: the estimated accuracy of the integral lists of Wells and Wilson is 10^{-10}; the latter authors elected to terminate their SCF calculations when an absolute accuracy of 10^{-8} was achieved in the elements of the density matrix. The most accurate calculations to date are the finite-element computations of Yang, Heinemann, and Kolb [30].

Two linear molecules with more than two electrons have been studied using RELMOL; these are the closed-shell HCl and HF systems; our results are tabulated and compared with other calculations in Tables II and III. Accurate nonrelativistic calculations for HCl have long been available [34]; these have been computed using Slater-type orbitals, which are very effective in studies of linear molecules. The first relativistic calculations to be performed on HCl are those due to Laaksonen, Grant, and Wilson [28], who also studied nonrelativistic limits; we have used larger basis sets than the latter authors, for which reason our nonrelativistic limits are in better agreement with the numerical estimates of Laaksonen, Grant, and Wilson [28], the Slater basis-set predictions of McLean and Yoshimine [34], and the Gaussian basis-set calculations of Wilson and Silver [31]. Our calculations for the ground-state energy of the HF system appear to be more accurate than our calculations for the ground state of HCl: our nonrelativistic limits differ by less than 2 mhartree from the finite-difference estimates of Laaksonen, Pyykkö, and Sundholm [32] and are comparable in accuracy with the Gaussian basis set calculations of Wilson and Silver [31].

Some relativistic and nonrelativistic calculations for the water molecule are presented in Table IV. Although there are small differences from the geometry and the nuclear model employed by other authors [18,35,36], the principal source of the disagreement between our calculations and others is, of course, the difference in the basis set. Our nonrelativistic limits—obtained by increasing the speed of light by a factor of 10^4—are seen to differ from the predictions of Ref. [35] by about 11 mhartree.

The ammonia molecule has also been studied. Our results are given in Table V. Our nonrelativistic limits—again obtained by increasing the speed of light by a factor of 10^4—are seen to differ by roughly 12 mhartree from the estimates of Hariharan and Pople [37]. Once again, the primary source of error is basis-set truncation.

Finally, the results of several calculations for the ground state of the methane molecule are collected in Table VI. Our calculations are quite inaccurate for the purposes of total-energy estimation as is evident from a comparison with the nonrelativistic estimate of Hariharan and Pople [37]. (Nonrelativistic limits from RELMOL are obtained by increasing the speed of light by a factor of 10^4.) Nonetheless, our nonrelativistic limits appear to be the most accurate for the purpose of determining the relativistic correction to the total energy: our basis set is larger than that of Aerts and Nieuwpoort [25], and Dyall *et al* [20] do not estimate relativistic corrections. Our estimate of the relativistic correction, $-0.015\,908$ hartree, is in good agreement with the perturbation theoretic estimate of Almlof and Faegri [38]: -0.0147 hartree at $R\approx 2.0466a_0$, where a_0 denotes the Bohr radius. As mentioned in Sec. II, we have used uncontracted basis sets. All other relativistic calculations for the methane molecule in Table VI make use of contracted basis sets. Contraction of Gaussian-type basis

TABLE II. Total energies (in hartrees) for the ground state of the HF molecule. Nuclei are assumed to be stationary point particles. The internuclear separation is $1.7328a_0$ in all calculations. In the footnote, the notation d: 2–5, for instance, means that the exponents for the $\bar{d}$ and d symmetries are $\xi_2,\ldots,\xi_5$, where $\xi_i=ab^{i-1}$.

	Calculation	U
$c=137.035\,989\,5$	F: $22s/16p/4d/1f$; H: $11s/4p/1d$[a]	$-100.161\,647\,794$
$c\rightarrow 10^4c$	F: $22s/16p/4d/1f$; H: $11s/4p/1d$[a]	$-100.069\,744\,366$
Nonrelativistic	Wilson and Silver [31]	$-100.069\,30$
	Laaksonen, Pyykkö, and Sundholm [32]	$-100.070\,82$

[a] RELMOL calculation: $a=0.176\,789\,366\,295\,209$ and $b=2.117\,095\,464\,905\,02$. For F, s: 1–22 [33], p: 1–16, d: 2–5, and f: 3–3; for H, s: 1–11, p: 2–5, and d: 3–3.

TABLE III. Total energies (in hartrees) for the ground state of the HCl molecule. Nuclei are assumed to be stationary point particles. The internuclear separation R is measured in Bohr radii. The notation used in the footnotes to the present table is explained in the caption of Table II.

	Calculation	U
	$R=2.40$	
$c=137.035\,989\,5$	Cl: $22s/16p/4d/14f$; H: $11s/4p/1d$[a]	$-461.567\,080\,695$
$c\rightarrow 10^4c$	Cl: $22s/16p/4d/1f$; H: $11s/4p/1d$[a]	$-460.110\,918\,296$
$c=137.037\,3$	Cl: $10s/6p$; H: $7s/4p$[b]	$-461.525\,38$
$c=10^4$	Cl: $10s/6p$; H: $7s/4p$[b]	$-460.060\,81$
$c=10^7$	Cl: $10s/6p$; H: $7s/4p$[b]	$-460.060\,54$
Nonrelativistic	Laaksonen, Grant, and Wilson [28]	$-460.113\,05$
	$R=2.4087$	
$c=137.035\,989\,5$	Cl: $22s/16p/4d/1f$; H: $11s/4p/1d$[a]	$-461.567\,037\,586$
$c\rightarrow 10^4c$	Cl: $22s/16p/4d/1f$; H: $11s/4p/1d$[a]	$-460.110\,876\,180$
Nonrelativistic	McLean and Yoshimine [34]	$-460.111\,85$
	Wilson and Silver [31]	$-460.110\,91$

[a] RELMOL calculation: $a=0.133\,470\,351\,130\,481$ and $b=2.175\,839\,165\,810\,64$. For Cl, s: 1–22 [33], p: 1–16, d: 2–5, and f: 3–3; for H, s: 1–11; p: 2–5, and d: 3–3.

[b] Reference [28].

TABLE IV. Total energies (in hartrees) for the ground state of the H_2O molecule. The notation used in the footnotes to the present table is explained in the caption of Table II.

Calculation	U^R	U^{NR}
O: $4s/2p$; H: $2s$[a]	$-75.168\,415$	$-75.120\,506$
O: $28s/18p/8d/3f$; H: $18s/8p/3d$[b]		$-76.067\,417$
O: $11s/7p/1d$; H: $6s/1p$	$-76.109\,453$[c]	$-76.054\,402$[d]
O: $12s/8p/3d$; H: $6s/3p$[e]	$-76.110\,988\,887\,0$	$-76.055\,826\,533\,8$

[a] Reference [18]; H—O, 0.96 Å; H—O—H, 104.5°.

[b] Reference [35]; equlibirum geometry; point nuclei.

[c] Reference [36]; H—O, 0.939 020 Å (1.774 49a_0); H—O—H, 107.68°; finite nuclei.

[d] Reference [36]; H—O, 0.939 051 Å (1.774 55a_0); H—O—H, 107.75°; finite nuclei.

[e] RELMOL calcuation: H—O, 0.958 Å; H—O—H, 104.45°; point nuclei; $a=0.231\,424\,578\,379\,716$ and $b=2.775\,712\,086\,258\,40$. For O, s: 1–12 [33], p: 1–8, and d: 2–4; for H, s: 1–6 and p: 2–4.

TABLE V. Total energies (in hartrees) for the ground state of the NH_3 molecule. Nuclei are assumed to be stationary point particles. The notation used in the footnotes to the present table is explained in the caption of Table II.

Calculation	U^R	U^{NR}
HF limit[a]		-56.225
N: $12s/8p/2d$; H: $6s/1p$[b]	$-56.243\,968\,487\,6$	$-56.212\,958\,187\,5$

[a] Reference [37]; N—H, 1.913a_0.

[b] RELMOL calculation: N—H, 1.008 Å$\approx 1.905a_0$; $a=0.175\,805\,843\,340\,089$ and $b=2.783\,763\,706\,577\,34$. For N, s: 1–12 [33], p: 1–8, and d: 2–3; for H, s: 1–6 and p: 2–2.

TABLE VI. Total energies (in hartrees) for the ground state of the CH_4 molecule. Nuclei are stationary. The notation used in the footnotes to the present table is explained in the caption of Table II.

Calculation	U^R	U^{NR}
HF limit[a]		−40.225
C: $12s/7p \rightarrow 8s/4p$; H: $6s \rightarrow 4s$[b]	−40.207 87	−40.191 88
C: $11s/6p/2d \rightarrow 5s/4p/2d$; H: $5s/1p \rightarrow 3s/1p$[c]	−40.228 306	
C: $10s/7p/2d$; H: $5s/2p$[d]	−40.225 444 149 1	−40.209 535 717 5

[a] Reference [37]; C—H, 2.050a_0; point nuclei.

[b] Reference [25]; C—H, 2.061 73a_0; point nuclei.

[c] Reference [20]; C—H, 2.0446a_0; finite nuclei.

[d] RELMOL calculation: C—H, 1.091 Å≈2.061 67a_0; point nucleus; $a = 0.150\,448\,678\,144\,222$ and $b = 3.075\,349\,900\,990\,60$. For C, s: 1–10 [33], p: 1–7, and d: 2–3; for H, s: 1–5 and p: 2–3.

functions has often been used to reduce their number and hence the number of two-electron integrals. We refer the reader elsewhere [39] for a recent examination of issues related to the use of contracted basis sets in relativistic calculations.

IV. CONCLUSION

We have described a Dirac-Fock procedure for closed-shell molecular systems or one-electron molecular ions; nuclei have been modeled as point particles; no account is taken of nuclear motion. The Dirac-Fock procedure has been implemented in a suite of programs. A number of molecular systems have been studied and provide evidence of the correctness of the procedure and its implementation.

We provide numerical evidence that adherence to strict kinetic balance at each center in a LCAO-MO approach based on spinor-spherical harmonic Gaussian-type basis functions is sufficient to ensure the upper-bound property of practical relativistic molecular electronic-structure calculations and that the flexibility inherent in geometric basis sets may be easily exploited to obtain accurate relativistic molecular energies. Relativistic models yield their nonrelativistic counterparts when the speed of light is increased to sufficiently large values. The approach is shown to be valid in a variety of geometries.

Although we have only treated molecules with light atoms, our test calculations provide evidence of the feasibility of performing relativistic calculations to any desired degree of accuracy for systems containing heavy atoms, provided adequate programming and computational resources are available. Revisions of our programs, based on the use of point group as well as time-reversal symmetry and the recursive generation of integrals, are in preparation. The exploitation of symmetry greatly facilitates the use of the larger basis sets required in reliable molecular electronic-structure calculations.

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