A finite-nucleus model for relativistic electronic structure calculations using a Douglas–Kroll-transformed Hamiltonian*

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Summary. We report the implementation of a Gaussian finite-nucleus model in the framework of the spin-free no-pair Hamiltonian obtained from the Douglas–Kroll transformation of the no-pair operator with external-field projectors. The finite nucleus regularizes the weak singularity of the wavefunction at the locations of the nuclei and provides a means for efficient exponent optimization using a spin-averaged relativistic one-component operator. We report and discuss basis sets for the gold atom obtained from various optimization procedures, making use of a point nucleus as well as employing various finite-nucleus models.

Key words: Douglas–Kroll transformation – Gaussian finite-nucleus model – Finite nucleus

1 Introduction

Computational models for atoms and molecules in the framework of the non-relativistic Schrödinger equation in the Born–Oppenheimer approximation usually employ a point-nucleus model for the external-potential term that describes the attraction of the electrons by the nuclei. Although the nucleus in reality has, of course, some finite extension, this model is in general considered justified, because the diameter of the nucleus is of the order of some femtometres, whereas the electrons most of the time move at a much larger distance of the order of picometres up to a few hundred picometres in the valence shell. Thus, the detailed charge distribution of the nucleus is expected to have negligible influence on the electronic energy and low-order moments of the electronic charge distribution. Moreover, a finite-nucleus model will necessarily have to introduce some assumptions and parameters pertinent to the specific model employed for the nuclear structure, and thus to some extent the well-defined mathematical structure of the point-nucleus model will be destroyed.

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The situation is different for relativistic models of electronic structure theory. It is well known that the solution of the one-particle Dirac–Coulomb equation for a point-nucleus external potential exhibits a weak singularity at the origin [1]. This property requires special attention in the practical calculation of a many-electron system when relativistic effects become important, as is the case already in the first transition-metal row. For atoms, a well-established method is at hand, namely the Dirac–Hartree–Fock (DHF) method based on a multi-particle generalization of the Dirac–Coulomb equation [2, 3] or, more precisely, on second-quantized generalizations thereof [4–6]. Usually, the problem of the weak singularity is handled in the corresponding computer codes [7, 8] by the introduction of a finite-nucleus model, although the fact that the DHF equations in the programs mentioned above are solved on a grid already provides a regularization mechanism that also permits to solve a point-nucleus model.

Problems with the singularity are probably more prominent in an expansion approach to the solution of the DHF equations: A basis set optimization, say in a basis of Gaussian functions, will lead to basis functions with very high exponents, thus trying to mimick the divergence at the origin by means of very steep Gaussians. These are clearly non-physical and unwanted in a practical calculation, since "grid points" in the functional space are set in a region that is not important for the properties one is usually interested in, and thus, at best, computational effort is wasted. It has therefore been proposed that a finite-nucleus model be used also in DHF calculations carried out by means of basis expansion techniques [9], in particular in a basis of Gaussian functions [10–12]. Note that a suitable choice of the finite-nucleus model, e.g., a uniformly charged sphere, leads to a harmonic potential at the origin. Thus, we expect rapid convergence of the basis set expansion, since Gaussian functions provide the correct asymptotic behaviour and are therefore ideally adapted to the problem [3, 10, 13].

An approach alternative to DHF, particularly useful for molecules, is the reduction of the DHF equations or their second-quantized analogue to operate only on the electronic degrees of freedom [14, 15]. Depending on the scheme that is being used, diverse problems arise in the case of an external field effected by a point nucleus.

In the Foldy–Wouthuysen approach [14], an expansion in powers of the reciprocal velocity of light is carried out, leading to increasingly singular operators [16], the lowest order of which is given by the so-called mass–velocity term

$$H_{mv} = -\frac{p^4}{8m^3c^2}, \tag{1}$$

and the Darwin term

$$H_D = \frac{\pi e\hbar^2}{2m^2c^2}\rho(r), \tag{2}$$

$\rho(r)$ denoting the nuclear charge distribution. The latter operator being itself extremely singular if a point nucleus, i.e., the nuclear charge distribution $\rho(r) = \delta(r)$, is used and the former one being not bounded from below, we have to face very unsatisfactory properties of the Foldy–Wouthuysen wavefunction, which have been investigated in detail by Kutzelnigg [17]. The individual terms exhibit considerable sensitivity to the model of the nucleus. This has been investigated for the expectation value of the Darwin term, using a Gaussian nucleus model [18], and also recently in a study that also pays attention to the influence of the nuclear model on the spin–orbit operator and the mass–velocity term [19].

The Douglas–Kroll transformation [15] does not lead to singular operators like Eqs. (1) or (2), since an expansion of the relativistic free-particle energy operator

$$E = \sqrt{p^2 c^2 + m^2 c^4}, \tag{3}$$

which is the reason for the weird spectral properties of (1), is not attempted. Instead, Douglas and Kroll expand in powers of the external Coulomb potential, thus arriving at a sum of operators, each one not more singular at the origin than the Coulomb potential itself. The Douglas–Kroll-transformed Hamiltonian is thus suitable for practical calculations, making it easy to implement electron correlation in a spin-free formalism [20, 21] and also in approaches including spin–orbit coupling [22].

A straightforward basis set optimization with the spin-free no-pair operator, using a linear combination of atom-centered Gaussians to expand its solution, leads to high exponents very similar to the DHF case discussed above. In this publication we therefore describe the implementation of a finite-nucleus model in the framework of the Douglas–Kroll transformation. We take the gold atom as an example and develop a "relativistic" basis set, starting from a $17s\,12p8d4f$ Gaussian basis set optimized with the non-relativistic Schrödinger Hamiltonian [23] by means of exponent optimization with the relativistic operator in combination with the finite-nucleus model.

In the following section we briefly review the Douglas–Kroll transformation and the finite-nucleus model. We proceed to a description of our implementation of the required integrals and then present practical calculations, introducing the new basis set and comparing our findings with DHF results obtained with the GRASP code (General-Purpose Relativistic Atomic Structure Program) [8].

2 Theory

2.1 The relativistic Hamiltonian

We employ the spin-free no-pair Hamiltonian with external-field projectors, derived from the second-quantized no-pair Hamiltonian [6] by means of a Douglas–Kroll transformation [15]. Assuming that a spin-averaged description is appropriate for the case to be considered and that spin–orbit coupling may be treated by perturbation theory at a later stage, we obtain a Hamiltonian operating on a one-component (properly antisymmetrized) wavefunction:

$$H^{\text{sf}2} = \sum_i E_i + \sum_i V^{\text{sf}}_{\text{eff}}(i) + \sum_{i<j} V^{\text{sf}}_{\text{eff}}(i,j), \tag{4}$$

with E_i the relativistic free-particle kinetic energy operator of Eq. (3), evaluated for the ith electron, and $V^{\text{sf}}_{\text{eff}}(i)$ and $V^{\text{sf}}_{\text{sff}}(i,j)$ the one- and two-particle potential energy operators that include spin-free relativistic corrections. Since the relativistic corrections of the two-electron potential are not of importance in the present context and can be shown to be of negligible influence in the calculation of valence-shell energies of atoms [21], we neglect then in the sequel and rather consider one-electron corrections only, using

$$H^{\text{sf}1} = \sum_i E_i + \sum_i V^{\text{sf}}_{\text{eff}}(i) + \sum_{i<j} \frac{1}{r_{ij}} \tag{5}$$

as the relativistic Hamiltonian.

Putting the velocity of light $c \equiv 1$, the one-electron (nuclear attraction) potential for electron i is given by

$$V_{\text{eff}}^{\text{sf}}(i) = -eA_i[V_{\text{ext}}(i) + \mathbf{R}_i V_{\text{ext}} \mathbf{R}_i]A_i \tag{6}$$

$$- W_1^{\text{sf}}(i)E_i W_1^{\text{sf}}(i) - \tfrac{1}{2}\{(W_1^{\text{sf}})^2, E_i\}, \tag{7}$$

with

$$A_i = \sqrt{\frac{E_i + m}{2E_i}} \tag{8}$$

and

$$R_i = \frac{\mathbf{p}_i}{E_i + m}. \tag{9}$$

$W_1^{\text{sf}}(i)$ is an integral operator with kernel

$$\mathscr{W}_1^{\text{sf}}(\mathbf{p}_i, \mathbf{p}_i') = A_i(\mathbf{R}_i - \mathbf{R}_i')A_i' \frac{V_{\text{ext}}(\mathbf{p}_i, \mathbf{p}_i')}{E_i + E_i'}. \tag{10}$$

This operator is evaluated from the matrix elements of the external potential $V_{\text{ext}}(i)$ between Gaussian functions by means of a matrix technique described elsewhere [21]. Thus, the implementation of a finite-nucleus model requires modification of the one-electron Coulomb integrals only, which may subsequently be subjected to the matrix technique for the evaluation of $V_{\text{eff}}^{\text{sf}}$.

2.2 The finite-nucleus model

There are several models for the charge distribution of the nucleus known from literature. Ishikawa [10] used a uniformly charged sphere with a certain prescribed radius R^{nuc} of the dimension of a few femtometres. In the context of expansions into Gaussian orbitals it is, however, more convenient to use a Gaussian charge distribution for the nucleus [18, 11], normalized to integrate to the total nuclear charge and given by

$$\rho(r) = eZ\left(\frac{\eta}{\pi}\right)^{3/2} e^{-\eta r^2}. \tag{11}$$

The decay parameter η is to be connected with the nuclear radius via the standard deviation σ of the Gaussian or the root-mean-square radius R_{rms} of the Gaussian. Matrix elements of the corresponding potential in a basis of Gaussian functions are readily evaluated, also in the multicentre case. We therefore choose the Gaussian finite-nucleus model in our development.

The fixing of the width of the Gaussian is open to debate. Visser et al. [11] propose two methods: First, assume that the extent of the nucleus is given by the ansatz [24, 25, 7]

$$R = r_0 A^{1/3}, \tag{12}$$

with A the atomic mass and $r_0 = 2.27 \times 10^{-5}$, giving R in atomic units. We may then relate R with the standard deviation of the Gaussian by means of an adjustable parameter γ, $R = \gamma\sigma$.

Second, equate the experimental root-mean-square radius R_{rms}^{nuc} [26] to the rms radius of the Gaussian, leading to an expression for the exponent η given by

$$\eta = \tfrac{3}{2}(R_{rms}^{nuc})^{-2}. \tag{13}$$

The integrals of the potential caused by a Gaussian charge distribution may be expressed in a form that makes it possible to use conventional two-electron integral routines for the calculation of its matrix elements between Gaussian functions [11]. However, in the case considered in the present paper, we prefer to reduce the required integrals directly to simple formulae for the one-electron integrals.

The potential of a charge distribution given by Eq. (11) centred at a point P at a distance R from this distribution is given by

$$V(r) = -\frac{eZ}{r}\Phi(\sqrt{\eta}r), \tag{14}$$

where the error function Φ is defined by

$$\Phi(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\,dt. \tag{15}$$

To evaluate the one-centre nuclear attraction using a finite-nucleus model making use of a Gaussian charge distribution, we have to calculate the integral

$$I = \int_{-\infty}^{\infty}\phi_i(x)\phi_i(x)\,V(r)\,d^3x. \tag{16}$$

The parameters l_i, m_i, n_i and α_i characterize the ith function in the Gaussian basis set:

$$\phi_i = N_i x^{l_i} y^{m_i} z^{n_i} e^{-\alpha_i r^2}, \quad r = |x|. \tag{17}$$

Defining $2p = l_1 + l_2 + m_1 + m_2 + n_1 + n_2$ and $\delta = \alpha_1 + \alpha_2$, we employ polar coordinates, isolate the angular part J and obtain

$$I = J \cdot \frac{2N_1 N_2}{\sqrt{\pi}}\int_0^{\infty} r^{2p} e^{-\delta r^2}\left[\frac{\sqrt{\pi}}{2}\Phi(\sqrt{\eta}r)\right]r\,dr \tag{18}$$

$$\equiv J \cdot N_1 N_2 I_p(\sqrt{\eta}, \delta). \tag{19}$$

With the result

$$I_0(\sqrt{\eta}, \delta) = \frac{\sqrt{\eta}}{2\delta(\delta + 1)^{1/2}}, \quad \operatorname{Re}\delta > -\eta, \operatorname{Re}\delta > 0, \tag{20}$$

it is straightforward to get the working equations

$$I_1(\sqrt{\eta}, \delta) = \frac{\sqrt{\eta}(3\delta + 2\eta)}{4\delta^2(\delta + \eta)^{3/2}}, \tag{21}$$

$$I_2(\sqrt{\eta}, \delta) = \frac{\sqrt{\eta}}{8\delta^3(\delta + \eta)^{5/2}}[15\delta^2 + 20\delta\eta + 8\eta^2], \tag{22}$$

$$I_3(\sqrt{\eta}, \delta) = \frac{\sqrt{\eta}}{16\delta^4(\delta + \eta)^{7/2}}[105\delta^3 + 210\delta^2\eta + 168\delta\eta^2 + 48\eta^3] \tag{23}$$

and

$$I_4(\sqrt{\eta}, \delta) = \frac{\sqrt{\eta}}{32\delta^5(\delta + \eta)^{9/2}} [945\delta^4 + 2820\delta^3\eta + 3024\delta^2\eta^2$$
$$+ 1728\delta\eta^3 + 384\eta^4] . \tag{24}$$

3 Results and discussion

As a first application of the finite-nucleus model within our relativistic scheme we report an exponent optimization of a $17s12p8d4f$ basis set for the gold atom, optimized previously by means of a straightforward exponent variation at the non-relativistic SCF (self-consistent field)-Hartree–Fock level [23], making use of a procedure and an SCF code for atoms known from the literature [27–29]. The optimization proceeds by direct variation of exponents and a search for a minimum of the total energy by means of a fit of the calculated values to a polynomial. After several cycles over all single exponents, a multidimensional (numerical) determination of the minimum is attempted. This process is repeated until the change in total energy is less than 10^{-5} Hartrees.

In our instance we employ the same code, modified to comprise the spin-free no-pair operator with external-field projectors and the Gaussian finite-nucleus model as described in Sect. 2. We start our optimization with the nonrelativistic $17s12p8d4f$ basis set published earlier, which we tabulate again for reference in Table 1, along with the results of the relativistic optimization.

We use two different ansätze for the exponent η in Eq. (12), the first one based on the experimental rms radius of the ^{197}Au nucleus with $R_{exp}^{rms} = 5.3$ fm being used for the optimization. The second value of $R_{nuc}^{rms} \approx 6.36$ fm corresponding to a 20% increase of the rms radius, has been provided in order to give a feeling for the influence of the nuclear radius.

Moreover, we attempted an exponent optimization with the relativistic operator and the point-nucleus model. In this instance it did not turn out possible to obtain a set of exponents describing a stationary point of the energy with respect to exponent variation, the total energy still decreasing in the third digit after the decimal point for the exponents given in Table 1.

An inspection of this table shows that the exponent optimization procedure making use of the point nucleus indeed tries to describe a singularity at the origin within the restrictions of a finite basis set, as the highest exponents in the space of s functions developed to about 50 times the value we started out with. Clearly, this method of exponent optimization is not a feasible one, since it will not converge to a stage with an essentially stationary result. Moreover, as discussed in the introduction, the large exponents are not required to describe the medium range of the wave function, which is determining the value of the energies, and also immaterial for such first-order properties that depend on a low (absolute) power of the distance from the nucleus, as many of the interesting properties do.

On the other hand, the optimization procedure with the Gaussian nucleus converged to a set of exponents corresponding to a point with a, for practical purposes, stationary energy. The resulting exponents obtained with $R_{nuc}^{rms} = 5.3$ fm are also given in Table 1.

We observe that the inner (and outer) s exponents are larger than their non-relativistic counterparts, as one should expect from the general properties of a relativistic orbital, but in this instance only by a factor of 10 for the highest

Table 1. Exponents of the $(17s12p8d4f)$ basis set for the gold atom

Non-relativistic optimization point nucleus	Relativistic optimization point nucleus	Relativistic optimization Gaussian nucleus
s exponents		
3095420.0	166643000.0	29077400.0
446260.0	17991400.0	4665930.0
99928.8	3180390.0	1059530.0
28274.9	715743.0	281273.0
9358.39	187598.0	84311.2
3491.38	54984.4	27756.7
1429.50	17640.7	9845.95
621.277	6088.72	3713.94
233.439	2229.58	1482.82
113.614	855.227	627.142
58.4805	286.375	241.530
26.2455	122.841	108.298
13.3527	37.2398	34.6885
5.15347	19.9257	16.49687
1.64510	6.16327	6.091290
0.730473	1.08749	1.087940
0.054579	0.078608	0.086209
p exponents		
23072.8	134701.0	113988.0
5459.12	20969.3	18303.6
1773.84	5072.08	4556.52
677.791	1561.95	1434.59
285.457	559.21	520.969
127.800	220.278	206.811
55.2681	91.4179	85.0870
26.1332	38.6095	36.6366
10.7993	16.1506	15.0214
4.95651	6.65501	6.39604
1.56922	1.96030	1.87306
0.580380	0.737265	0.704253
d exponents		
816.722	933.897	944.088
243.203	267.029	268.492
90.5378	97.077	97.1813
36.8619	38.8019	38.7422
14.0038	14.5881	14.5075
5.54660	5.70114	5.67105
1.51102	1.52155	1.51099
0.429674	0.42022	0.416578
f exponents		
86.8244	85.719	85.7235
27.7504	27.0547	27.0580
9.91205	9.55937	9.56122
3.33817	3.16991	3.17190

exponent. We expect higher exponents in the relativistic finite-nucleus case, since the relativistic s orbital in this instance has considerably larger amplitude for small distances from the nucleus than its nonrelativistic counterpart [9]. The p exponents are likewise shifted corresponding to a tighter charge distribution, whereas the outer d and f exponents describe a slightly more diffuse charge distribution than in the non-relativistic case, again in line with the expectations derived from known relativistic effects on orbital radii.

The total energies, orbital energies, $\langle r^2 \rangle$ and $\langle r^{-1} \rangle$ expectation values are given for some inner-shell and the valence-shell orbitals in Tables 2–4. The data obtained from the GRASP program will be used as a benchmark. Note that the point-nucleus values differ slightly from those published in [23], since in this publication a molecular code making use of six-component cartesian d functions and ten-component cartesian f functions has been employed, whereas in the present case contaminants are not present.

A comparison of the numerical nonrelativistic results with the basis set results shows that despite a quite satisfactory total energy, orbital energies and charge distributions calculated with the optimized $17s12p8d4f$ non-relativistic point-nucleus basis set [23] show errors of the order of 10%, which is quite unacceptable. This deficiency may be traced to inflexibility in the valence shell, in particular of the d and f symmetries. From Table 2 we find that already the inclusion of a semidiffuse d function with exponent 0.11 bohr^{-2} leads to considerable improvement. This function may not be obtained by optimization of the total energy at the Hartree–Fock level, because its influence on the total energy is negligible, and a straightforward optimization with an additional d function rather shifts the values of the d space uniformly to higher values, which leads to lower energies for the inner-shell d orbitals.

The semidiffuse function has instead been determined by optimizing the *correlated* ground state energy of the Au ^2S state, and in fact it has been known for a long time that for satisfactory calculations on transition metals a semidiffuse d function, often dubbed Hay's d function [30], has to be included at the correlated level. This function turns out to be of importance even at the SCF level, and its large (indirect) influence even on the 6s shell is remarkable. The orbital energies (except for the 4f shell, which still lacks some flexibility) are now in very good agreement (better than 1%) with the benchmark results.

The $\langle r^2 \rangle_{6s}$ expectation value, however, still indicates deficiencies in the s shell. This is also reflected in the ionization potentials and electron affinities calculated with this basis set [23]. In order to overcome these problems, we introduced in a recent paper [31] a more flexible basis set, which is obtained from the nonrelativistic one given in Table 1 by deleting all functions with exponents less than 3 bohr^{-2} and augmenting this set by an approximately even-tempered series of exponents providing a flexible valence shell. The latter exponents are given in Table 5, and we have included also results for this extended basis set in Tables 2–4. It is obvious that this basis set (dubbed NRPx) shows excellent agreement with GRASP results.

We employ the same recipe as described above to generate extended basis sets RPx and RGx for the optimization carried out in the framework of a relativistic point nucleus and a relativistic Gaussian nucleus. The nonrelativistic calculations employing a Gaussian nucleus show practically no difference to the point-nucleus results, corroborating the expectation that a point-nucleus theory is quite adequate in this case.

We now turn to a discussion of the result obtained from relativistic scalar calculations. The relativistic contraction of the s and p orbitals and the expansion

Table 2. Numerical and basis set calculations on the gold atom

	Total energy	$-\varepsilon_{1s}$	$-\varepsilon_{2s}$	$-\varepsilon_{5s}$	$-\varepsilon_{6s}$	$-\varepsilon_{4f}$	$-\varepsilon_{5p}$	$-\varepsilon_{5d}$
GRASP results – nonrelativistic – numerical Hartree-Fock solution								
Point nucleus	−17865.4001	2706.8	457.18	3.8088	0.22078	4.3283	2.5343	0.52102
Gaussian nucleus[a]	−17864.8211	2706.6	457.16	3.8086	0.22076	4.3284	2.5344	0.52104
GRASP results – relativistic – numerical Dirac–Hartree–Fock solution								
Point nucleus	−19039.8444	2987.9	532.44	4.6873	0.29193	3.8676 / 3.7203	3.1894 / 2.5588	0.49340 / 0.42862
Uniform charge nucleus[a]	−19037.1198	2986.8	532.28	4.6855	0.29177	3.8606 / 3.7206	3.1894 / 2.5589	0.49348 / 0.42870
Gaussian nucleus[a]	−19035.7636	2986.3	532.20	4.6846	0.29168	3.8680 / 3.7207	3.1894 / 2.5590	0.49353 / 0.42874
Gaussian nucleus[b]	−19034.3662	2985.6	532.12	4.6837	0.29160	3.8682 / 3.7209	3.1894 / 2.5591	0.49357 / 0.42878
This work – nonrelativistic calculation with point nucleus								
NRP[c]	−17863.9093	2706.7	457.09	3.7285	0.19987	4.1631	2.4601	0.44925
RP[d]	−17863.1050	2706.5	456.88	3.5741	0.17702	4.0354	2.3929	0.39831
NRP + d(0.11)	−17863.9777	2706.8	457.19	3.8207	0.22078	4.2654	2.5462	0.52236
NRPx[e]	−17864.2735	2706.9	457.28	3.8140	0.22098	4.3186	2.5388	0.52062
This work – nonrelativistic calculation with finite nucleus								
NRP	−17863.3403	2706.4	457.06	3.7282	0.19986	4.1632	2.4601	0.44926
This work – relativistic calculation with point nucleus								
NRP	−18988.8121	2975.0	530.85	4.5804	0.24269	3.6061	2.6673	0.39020
NRP + d(0.12)	−18988.9053	2975.2	530.98	4.7014	0.27166	3.7350	2.7783	0.48169
RP	−18991.6170	2975.8	530.95	4.5509	0.25123	3.5926	2.6419	0.36291
RG[f]	−18991.4844	2975.8	530.95	4.5475	0.25150	3.5909	2.6387	0.35820
NRPx[e]	−18989.2978	2975.2	531.07	4.6808	0.28971	3.7841	2.7494	0.45343
RPx[e]	−18992.1131	2976.1	531.19	4.6794	0.28938	3.7858	2.7491	0.45376
RGx[e,f]	−18991.9602	2976.0	531.18	4.6803	0.28951	3.7847	2.7496	0.45363

Table 2. (Continued)

This work – relativistic calculation with finite nucleus

	Total energy	$-\varepsilon_{1s}$	$-\varepsilon_{2s}$	$-\varepsilon_{5s}$	$-\varepsilon_{6s}$	$-\varepsilon_{4f}$	$-\varepsilon_{5p}$	$-\varepsilon_{5d}$
NRP	−18986.7366	2974.2	530.72	4.5791	0.24262	3.6063	2.6676	0.39024
RP	−18988.7357	2975.7	530.78	4.5489	0.25111	3.5927	2.6419	0.36293
RG[f]	−18988.8131	2974.7	530.78	4.5457	0.25137	3.5911	2.6387	0.35821
RG[g]	−18987.7070	2974.2	530.71	4.5449	0.25132	3.5911	2.6388	0.35822
RGX[e,f]	−18989.2889	2974.9	531.02	4.6785	0.28935	3.7850	2.7497	0.45370

[a] rms radius = 5.3 fm.
[b] rms radius = 6.36 fm.
[c] Basis set optimized for nonrelativistic point-nucleus calculation.
[d] Basis set optimized for relativistic point-nucleus calculation.
[e] Extended basis set (see text)
[f] Basis set optimized for relativistic Gaussian nucleus calculation (rms radius = 5.3 fm).
[g] Basis set optimized for relativistic Gaussian nucleus calculation (rms radius = 5.3 fm), but rms radius of 6.36 fm used.

Table 3. Numerical and basis set calculations on the gold atom

	$\langle r^2 \rangle_{1s}$	$\langle r^2 \rangle_{2s}$	$\langle r^2 \rangle_{5s}$	$\langle r^2 \rangle_{6s}$	$\langle r^2 \rangle_{4f}$	$\langle r^2 \rangle_{5p}$	$\langle r^2 \rangle_{5d}$
GRASP results – nonrelativistic – numerical Hartree–Fock solution							
Point nucleus	0.4907×10^{-3}	0.7629×10^{-2}	1.213	0.1589×10^{2}	0.2814	1.451	2.834
Gaussian nucleus[a]	0.4908×10^{-3}	0.7630×10^{-2}	1.213	0.1589×10^{2}	0.2814	1.451	2.834
GRASP results – relativistic – numerical Dirac–Hartree–Fock solution							
Point nucleus	0.3929×10^{-3}	0.5929×10^{-2}	0.9980	0.1085×10^{2}	0.2926 / 0.3006	1.178 / 1.408	2.821 / 3.153
Uniform charge nucleus[a]	0.3931×10^{-3}	0.5932×10^{-2}	0.9983	0.1086×10^{2}	0.2926 / 0.3005	1.179 / 1.408	2.821 / 3.152
Gaussian nucleus[a]	0.3933×10^{-3}	0.5933×10^{-2}	0.9985	0.1086×10^{2}	0.2926 / 0.3005	1.179 / 1.408	2.820 / 3.152
Gaussian nucleus[b]	0.3934×10^{-3}	0.5935×10^{-2}	0.9986	0.1087×10^{2}	0.2926 / 0.3005	1.179 / 1.408	2.820 / 3.152
This work – nonrelativistic calculation with point nucleus							
NRP[c]	0.4907×10^{-3}	0.7628×10^{-2}	1.213	0.1541×10^{2}	0.2721	1.453	2.594
RP[a]	0.4908×10^{-3}	0.7633×10^{-2}	1.149	0.1070×10^{2}	0.2763	1.428	2.669
NRP + d(0.11)	0.4907×10^{-3}	0.7628×10^{-2}	1.209	0.1536×10^{2}	0.2720	1.444	2.884
NRPx[e]	0.4907×10^{-3}	0.7628×10^{-2}	1.211	0.1586×10^{2}	0.2837	1.448	2.833
This work – nonrelativistic calculation with finite nucleus							
NRP	0.4908×10^{-3}	0.7629×10^{-2}	1.213	0.1541×10^{2}	0.2721	1.453	2.594
This work – relativistic calculation with point nucleus							
NRP	0.3620×10^{-3}	0.5914×10^{-2}	1.005	0.1484×10^{2}	0.2822	1.339	2.655
NRP + d(0.12)	0.3620×10^{-3}	0.5914×10^{-2}	1.001	0.1473×10^{2}	0.2822	1.328	3.015
RP	0.3618×10^{-3}	0.5913×10^{-2}	0.9949	0.1083×10^{2}	0.2856	1.318	2.701
RG[f]	0.3618×10^{-3}	0.5912×10^{-2}	0.9969	0.1002×10^{2}	0.2856	1.323	2.711
NRPx[e]	0.3620×10^{-3}	0.5914×10^{-2}	0.9998	0.1094×10^{2}	0.2990	1.328	3.009
RPx[e]	0.3618×10^{-3}	0.5914×10^{-2}	1.002	0.1096×10^{2}	0.2991	1.328	3.008
RGx[e,f]	0.3618×10^{-3}	0.5913×10^{-2}	1.001	0.1096×10^{2}	0.2992	1.328	3.008

Table 3. (Continued)

	$\langle r^2 \rangle_{1s}$	$\langle r^2 \rangle_{2s}$	$\langle r^2 \rangle_{5s}$	$\langle r^2 \rangle_{6s}$	$\langle r^2 \rangle_{4f}$	$\langle r^2 \rangle_{5p}$	$\langle r^2 \rangle_{5d}$
This work – relativistic calculation with finite nucleus							
NRP	0.3622×10^{-3}	0.5916×10^{-2}	1.005	0.1484×10^2	0.2822	1.339	2.655
RP	0.3621×10^{-3}	0.5916×10^{-2}	0.9951	0.1083×10^2	0.2856	1.318	2.701
RG[f]	0.3621×10^{-3}	0.5915×10^{-2}	0.9971	0.1102×10^2	0.2856	1.323	2.711
RG[g]	0.3622×10^{-3}	0.5916×10^{-2}	0.9972	0.1102×10^2	0.2856	1.323	2.711
RGx[e,f]	0.3621×10^{-3}	0.5916×10^{-2}	1.002	0.1096×10^2	0.2991	1.328	3.008

[a] rms radius = 5.3 fm.
[b] rms radius = 6.36 fm.
[c] Basis set optimized for nonrelativistic point-nucleus calculation.
[d] Basis set optimized for relativistic point-nucleus calculation.
[e] Extended basis set (see text)
[f] Basis set optimized for relativistic Gaussian nucleus calculation (rms radius = 5.3 fm).
[g] Basis set optimized for relativistic Gaussian nucleus calculation (rms radius = 5.3 fm), but rms radius of 6.36 fm used.

Table 4. Numerical and basis set calculations on the gold atom

	$\langle r^{-1}\rangle_{1s}$	$\langle r^{-1}\rangle_{2s}$	$\langle r^{-1}\rangle_{5s}$	$\langle r^{-1}\rangle_{6s}$	$\langle r^{-1}\rangle_{4f}$	$\langle r^{-1}\rangle_{5p}$	$\langle r^{-1}\rangle_{5d}$
GRASP results – nonrelativistic – numerical Hartree–Fock solution							
Point nucleus	0.7844×10^2	0.1848×10^2	1.263	0.3374	2.513	1.152	0.8501
Gaussian nucleus[a]	0.7844×10^2	0.1848×10^2	1.263	0.3374	2.513	1.152	0.8501
GRASP results – relativistic – numerical Dirac–Hartree–Fock solution							
Point nucleus	0.9583×10^2	0.2356×10^2	1.440	0.4176	2.485 / 2.451	1.316 / 1.182	0.8614 / 0.8176
Uniform charge nucleus[a]	0.9573×10^2	0.2354×10^2	1.440	0.4174	2.485 / 2.451	1.316 / 1.182	0.8614 / 0.8176
Gaussian nucleus[a]	0.9569×10^2	0.2353×10^2	1.439	0.4173	2.485 / 2.451	1.316 / 1.182	0.8614 / 0.8176
Gaussian nucleus[b]	0.9564×10^2	0.2353×10^2	1.439	0.4173	2.485 / 2.451	1.316 / 1.182	0.8614 / 0.8176
This work – nonrelativistic calculation with point nucleus							
NRP[c]	0.7844×10^2	0.1848×10^2	1.261	0.3306	2.517	1.148	0.8565
RP[d]	0.7844×10^2	0.1848×10^2	1.395	0.4270	2.507	1.154	0.8469
NRP + d(0.11)	0.7844×10^2	0.1848×10^2	1.264	0.3325	2.517	1.151	0.8430
NRPx[e]	0.7844×10^2	0.1848×10^2	1.264	0.3376	2.504	1.153	0.8502
This work – nonrelativistic calculation with finite nucleus							
NRP	0.7843×10^2	0.1848×10^2	1.261	0.3306	2.517	1.148	0.8565
This work – relativistic calculation with point nucleus							
NRP	0.1069×10^3	0.2502×10^2	1.461	0.3488	2.476	1.213	0.8469
NRP + d(0.12)	0.1069×10^3	0.2502×10^2	1.448	0.3537	2.476	1.218	0.8298
RP	0.1072×10^3	0.2506×10^2	1.442	0.3993	2.471	1.220	0.8433
RG[f]	0.1072×10^3	0.2506×10^2	1.444	0.4159	2.471	1.219	0.8423
NRPx[e]	0.1069×10^3	0.2502×10^2	1.454	0.4167	2.458	1.223	0.8354
RPx[e]	0.1072×10^3	0.2506×10^2	1.454	0.4165	2.458	1.222	0.8355
RGx[e,f]	0.1072×10^3	0.2505×10^2	1.455	0.4166	2.458	1.223	0.8355

Table 4. (Continued)

	$\langle r^{-1}\rangle_{1s}$	$\langle r^{-1}\rangle_{2s}$	$\langle r^{-1}\rangle_{5s}$	$\langle r^{-1}\rangle_{6s}$	$\langle r^{-1}\rangle_{4f}$	$\langle r^{-1}\rangle_{5p}$	$\langle r^{-1}\rangle_{5d}$
This work – relativistic calculation with finite nucleus							
NRP	0.1068×10^3	0.2500×10^2	1.444	0.3487	2.476	1.213	0.8469
RP	0.1070×10^3	0.2503×10^2	1.442	0.3993	2.471	1.220	0.8433
RG^f	0.1070×10^3	0.2503×10^2	1.443	0.4159	2.471	1.219	0.8423
RG^g	0.1070×10^3	0.2502×10^2	1.443	0.4159	2.471	1.219	0.8423
RGx^{e,f}	0.1070×10^3	0.2503×10^2	1.454	0.4165	2.458	1.223	0.8355

[a] rms radius = 5.3 fm.
[b] rms radius = 6.36 fm.
[c] Basis set optimized for nonrelativistic point-nucleus calculation.
[d] Basis set optimized for relativistic point-nucleus calculation.
[e] Extended basis set (see text)
[f] Basis set optimized for relativistic Gaussian nucleus calculation (rms radius = 5.3 fm).
[g] Basis set optimized for relativistic Gaussian nucleus calculation (rms radius = 5.3 fm), but rms radius of 6.36 fm used.

Table 5. Valence-shell exponents for the extended basis sets

s functions	p functions	d functions	f functions
2.100	2.250	2.200	1.100
0.840	1.000	0.880	0.420
0.340	0.455	0.350	0.170
0.140	0.210	0.140	
0.050	0.100	0.056	
0.022	0.046		
0.010	0.020		

of the d and f shells is reproduced in all cases, comparing the corresponding calculations for a fixed basis set, but again the magnitude of the effect is underestimated using the RP and RG basis sets due to basis set inflexibility. This is mirrored especially in the poor result obtained with the relativistic point nucleus basis set in the nonrelativistic calculation, reflecting the optimization for a much more compact charge distribution. Again, the situation is much improved by inclusion of Hay's d function. The $\langle r^2 \rangle_{5d}$ value is now excellent, but $\langle r^{-1} \rangle_{5d}$ overshoots and shows, in line with the $\langle r^2 \rangle_{6s}$ result, that an extended basis set is required for quantitative agreement. Note, however, that $\langle r^2 \rangle_{6s}$ is well described by the RP basis set. The extended basis sets with either type of core basis set (NRPx, RPx, RGx) all lead to very good agreement with the benchmark results in the valence shell, and it is in fact not evident which one is superior.

For core orbitals the $\langle r^2 \rangle_{1s}$ is too small in all cases, and $\langle r^{-1} \rangle_{1s}$ and $\langle r^{-1} \rangle_{2s}$ are too large with either basis set. This result (and the comparatively large discrepancies for the DHF total energies and the inner-shell orbital energies) is due to the fact that the two-electron terms have not been corrected in the present calculation. This may be done in the framework of the Douglas–Kroll transformation, but will not change the valence-shell results considerably [21].

Finally, turning to the finite-nucleus calculations, we find results similar to those obtained for the point-nucleus calculations. The only notable exception is $\langle r^2 \rangle_{6s}$, which for the RG set is slightly different in both cases due to basis set deficiencies.

Summarizing our results, we find that for a flexible basis set the mode of optimization is immaterial. NRPx, PRx and RGx give all very good results. Of course, an optimization using the point nucleus is not advisable because of slow convergence and the development of unnecessarily high exponents, and thus for an optimization in the framework of a relativistic theory a finite nucleus should be used. Our results indicate, however, that a sufficiently flexible basis set based on a nonrelativistic exponent optimization is quite satisfactory.

4 Conclusion

The Gaussian nucleus model may be favourably used to devise a procedure for exponent optimization using the Douglas–Kroll-transformed no-pair Hamiltonian. A point-nucleus model used in this context does not lead to a convergent optimization procedure and develops very high exponents, just as known from Dirac–Hartree–Fock calculations.

The 17s12p8d4f basis set as obtained from the optimization procedure does not provide enough flexibility to yield orbital energies and $\langle r^n \rangle$ expectation values in satisfactory agreement with numerical (GRASP) benchmark calculations. We expect that this will be true until very large basis sets are used, because the important semidiffuse and diffuse functions are disfavoured by an optimization procedure based on the Hartree–Fock energy.

We rather propose to build a flexible valence basis set by means of an even-tempered series of exponents starting with a suitable outer-core exponent obtained in the optimization procedure. This recipe also allows for inclusion of correlation functions, negative ion functions and Rydberg functions, as needed for post-SCF calculations.

Proceeding along these lines, we obtained basis sets which yield values for valence shell data in very good agreement (better than 1%) with GRASP results. Inner-shell results in the relativistic case deteriorate because of the approximations that have been made, in particular the neglect of the relativistic correction of the two-electron integrals.

The three extended basis sets obtained in this way from the nonrelativistic, relativistic point nucleus and relativistic Gaussian nucleus basis set lead to very similar results in the relativistic calculations. We thus conclude that for calculations with the Douglas–Kroll-transformed no-pair Hamiltonian a relativistic optimization is not required (unless the valence basis set that can be afforded is small or only of medium size) and that a nonrelativistic basis set of moderate size for inner and outer core, augmented by a large and flexible valence-shell basis set, is sufficient to obtain valence orbital energies and $\langle r^n \rangle$ expectation values as well as other properties depending on the valence shell with excellent accuracy. This is in line with previous findings [31]. Note, however, that relativistic contraction coefficients are markedly different from their nonrelativistic counterparts and must be determined from a *relativistic* atomic SCF calculation.

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