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Analytical local electron-electron interaction model potentials for atoms

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Analytical local potentials for modeling the electron-electron interaction in an atom reduce significantly the computational effort in electronic structure calculations. The development of such potentials has a long history, but some promising ideas have not yet been taken into account for further improvements. We determine a local electron-electron interaction potential akin to those suggested by Green *et al.* [Phys. Rev. **184**, 1 (1969)], which are widely used in atom-ion scattering calculations, electron-capture processes, and electronic structure calculations. Generalized Yukawa-type model potentials are introduced. This leads, however, to shell-dependent local potentials, because the origin behavior of such potentials is different for different shells as has been explicated analytically [J. Neugebauer, M. Reiher, and J. Hinze, Phys. Rev. A **65**, 032518 (2002)]. It is found that the parameters that characterize these local potentials can be interpolated and extrapolated reliably for different nuclear charges and different numbers of electrons. The analytical behavior of the corresponding localized Hartree-Fock potentials at the origin and at long distances is utilized in order to reduce the number of fit parameters. It turns out that the shell-dependent form of Green's potential, which we also derive, yields results of comparable accuracy using only one shell-dependent parameter.

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I. INTRODUCTION

The search for local model potentials has a long history (cf. [1–3] for reviews) since they simplify electronic structure and scattering calculations significantly. With these potentials, Hartree-Fock-like equations for the determination of orbitals are easily solvable. Analytical local potentials, which depend only on one electronic coordinate, lead to homogeneous equations that are by construction not of the self-consistent-field type and, thus, need not be evaluated iteratively. The time-consuming evaluation of two-electron integrals is also avoided.

These model potentials, in particular those proposed by Green *et al.* [1,4,5] which will be described below, have been used for the calculation of electron-atom and atom-ion scattering [6–8], electron impact excitation and ionization [9–11], antiproton-atomic collisions [12], oscillator strengths [9] and electron-capture processes [13,14]. Further model potentials that were applied in recent scattering studies [15,16], have also been presented [17–19]. In addition, these potentials provide an efficient way to obtaining the starting functions for computationally more demanding calculations of the Hartree-Fock (HF) or post-Hartree-Fock type [20–22]. Analytical independent particle model potentials can also be used in phenomenological studies for the qualitative understanding of atomic properties [2,3]. The development of such accurate analytical model potentials is, thus, highly desirable.

In 1969 Green *et al.* [1] presented a very successful shell-independent model potential of simple analytical form. By using a Thomas-Fermi-Dirac energy functional, Green *et al.* obtained a semiempirical formula for atomic total energies. Poisson's equation was used in their approach to gain analytical expressions for the electron density. It was found that at least the 1*s* shell requires a separate treatment [23,24]. Later, Green made the proposition to adjust different potentials for different *l* quantum numbers [2], but this has never been carried out.

An extensive parametrization for nonrelativistic atomic structure calculations has been given by Green and coworkers [5,25], while the corresponding relativistic parameters are only available for a small number of neutral atoms [4]. Parameters for light negative ions were derived in 1980 [26]. Fits to Thomas-Fermi or Hartree-Fock-Slater screening functions, Hartree-Fock-Slater or HF energy eigenvalues and electron spectroscopy for chemical andalysis data [1,4], as well as to numerical potentials [26], which were obtained by using the optimized effective-potential method by Talman and Shadwick [27], have been performed. Moreover, variational minimization of total energy expectation values, which leads to a variational procedure with respect to the parameters of the model potential, has been used [5,25,28,29].

Suggestions for a refinement of the Green's potential for electron-atom scattering processes can be found in Refs. [30,31]. A Yukawa-type potential was used for similar purposes [32]. In a related study, an energy-dependent model potential for scattering calculations was obtained [33].

In this work, we explore those features of local model potentials, which have not yet been studied by Green *et al.*, namely, shell-dependent analytical potential functions that allow a systematic improvement of the potential ansatz. From a detailed analysis in Ref. [34] it appears obvious that *shell-dependent* analytical independent particle model potentials could yield improved orbitals and energy expectation values. Moreover, the large number of fit parameters in Green's potential should be greatly reduced—if possible—through the particular analytical form of the potential and an extensive use of analytically known constraints.

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The paper is organized as follows. In Sec. II the homogeneous HF and DFC (Dirac-Fock-Coulomb) equations are presented to demonstrate where exactly the local model potential enters. Section III deals with the proposition of a generalized model potential and introduces constraints for the model potential parameters. An analysis of the parametrized model potentials is carried out in Sec. IV. In addition, the accurate, shell-independent Green potential is given in its shell-dependent form in Sec. IV D.

II. HOMOGENEOUS SCF EQUATIONS

The HF equations for atoms can be written in homogeneous form

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l_i(l_i+1)}{2r^2}+V_{\rm nuc}(r)+W_i^S(r)-\epsilon_i\right)P_i(r)=0, \tag{1}$$

where $W_i^S(r)$ represents the quasilocal HF electron-electron interaction potential (EEIP) (compare Ref. [34] for details), which shall be replaced by a model potential.

In DFC theory we have analogously

$$\begin{pmatrix} V_{\rm nuc}(r)+W_i^P(r)-\epsilon_i & A_i^\dagger(r) \\ A_i(r) & V_{\rm nuc}(r)+W_i^Q(r)-2c^2-\epsilon_i \end{pmatrix} \times\begin{pmatrix} P_i(r) \\ Q_i(r)\end{pmatrix}=\begin{pmatrix}0\\0\end{pmatrix}, \tag{2}$$

with

$$A_i(r)=c\left(\frac{d}{dr}+\frac{\kappa_i}{r}\right) \text{ and } A_i^\dagger=-c\left(\frac{d}{dr}-\frac{\kappa_i}{r}\right). \tag{3}$$

Here, $W_i^P(r)$ and $W_i^Q(r)$ are the contributions resulting from the electron-electron interaction. The situation here is more difficult than in the nonrelativistic case, since two components of the total EEIP have to be considered, which need not be equal for a given shell [34].

III. ANALYTICAL INDEPENDENT PARTICLE MODEL POTENTIALS

A. The Green potential

The analytical local model potential presented by Green *et al.* in 1969 has the form

$$V^{\rm Green}(r)=\frac{(N-1)}{r}\left[1-\frac{\xi}{\eta[\exp(\xi r)-1]+\xi}\right], \tag{4}$$

where N is the number of electrons, r is the radial variable, and ξ and η are adjustable parameters, which show a near-linear dependence on the nuclear charge Z for a given N [5],

$$\xi(N,Z)=\xi_0(N)+\xi_1(N)[Z-N], \tag{5}$$

$$\eta(N,Z)=\eta_0(N)+\eta_1(N)[Z-N]. \tag{6}$$

The asymptotic behavior of the potential is

$$\lim_{r\to\infty}V^{\rm Green}(r)=\frac{N-1}{r}, \tag{7}$$

which resembles the Coulomb interaction of an electron with the remaining cation at large distances (provided that the electron-nucleus potential is added) [27,35]. The series expansion of the potential at the origin yields

$$\lim_{r\to 0}V^{\rm Green}(r)=(N-1)\eta\Bigg[1+\frac{1}{2}(-2\eta+\xi)r+\frac{1}{6}(6\eta^2-6\eta\xi+\xi^2)r^2-\frac{1}{24}(24\eta^3-36\eta^2\xi+14\eta\xi^2-\xi^3)r^3+O(r^4)\Bigg]. \tag{8}$$

The value of this potential at the origin $V^{\rm Green}(0)=(N-1)\eta$ may be chosen such that η reproduces the origin behavior of the HF- and DFC-EEIPs, though this option has never been used due to the lack of analytical expressions for HF- and DFC-EEIPs at the origin. With the analysis given in Ref. [34] this can be overcome. In addition, a shell-dependent model can be introduced, as demanded by the analysis of the origin behavior of the HF-EEIPs [34]. Therefore, we determine shell-dependent values of η_i such that

$$\eta_i=\frac{1}{N-1}W_i^S(0), \tag{9}$$

to obtain

$$V_i^{\rm Green}(0)=W_i^S(0). \tag{10}$$

The index i denotes the shell dependence of this potential (i is a composite index for the $\{n_i,l_i\}$ set of quantum numbers). Note that Eq. (9) reduces the number of independent fit parameters in Eq. (4) by a factor of 1/2. We derived a shell-dependent set of optimized parameters ξ_i for the Green potential, which are the only freely adjustable parameters remaining. We refer to Sec. IV D for details on this parametrization since we would like to proceed in order to discuss the implications of shell dependence and fixed origin behavior for systematically improvable analytical model potentials.

B. A generalized model potential

Since the analytical form of the Green potential does not allow us to systematically improve on it, we step back to a Yukawa-type potential (cf. Ref. [28] for similar potentials),

$$V_i^{\rm GAMP}(r)=\frac{N-1}{r}\sum_{k=0}^{k_{max}}a_{k,i}\exp(-\alpha_k\xi_i r), \tag{11}$$

as a generalized analytical model potential (GAMP). The summation can be systematically extended to higher terms. In general, we take $\alpha_k=k$. Because of zero or slightly negative slopes of the HF-EEIPs, Gauss-type functions, $\exp(-\beta_\kappa\xi_i r^2)$, may be added, but tests have not shown any significant improvement. Since a shell-dependent potential is considered, all parameters depend on the quantum numbers and, additionally, on the nuclear charge Z and the number of electrons N,

$$\xi_i=\xi(Z,N,n_i,l_i), \tag{12}$$

$$a_{k,i}=a_k(Z,N,n_i,l_i). \tag{13}$$

Note that the parameters ξ_i in the above formula are not identical to Green's ξ. The shell dependence increases the number of parameters largely. Therefore, it is mandatory to find efficient interpolation formulas to reduce the number of parameters to the largest extent. We come back to this aspect in Sec. IV B.

The long-range behavior of the GAMP is given by

$$\lim_{r\to\infty} V_i^{\mathrm{GAMP}}(r)=\frac{N-1}{r}a_{0,i}. \tag{14}$$

Since the correct asymptotic form of the EEIPs, $\lim_{r\to\infty}W(r)=(N-1)/r$ must be reproduced, we obtain $a_{0,i}=1$ as a first constraint on the GAMP parameters. In the short-range limit, a Taylor series expansion of Eq. (11) yields

$$V_i^{\mathrm{GAMP}}(r)=\frac{N-1}{r}\sum_{k=0}^{k_{max}} a_{k,i}\left[1-k\xi_i r+\frac{k^2\xi_i^2}{2}r^2+O(r^3)\right]. \tag{15}$$

Since a singularity at the origin must not occur according to the results for the origin behavior for the HF-EEIPs in Ref. [34],

$$W_i^S(0)=\langle 1/R\rangle-\langle\rho_{ii}/r\rangle -\frac{1}{2}\sum_{j,l_j\leqslant l_i} D_j A_{ij(l_i-l_j)}^{HF}\langle\rho_{ij}/r^{l_i-l_j+1}\rangle\frac{a_{0,j}^{HF}}{a_{0,i}^{HF}}, \tag{16}$$

where we used the definition of the expectation value

$$\langle 1/R\rangle=\sum_i D_i\langle\rho_{ii}/r\rangle,\qquad \rho_{ii}=P_i(r)\cdot P_i(r), \tag{17}$$

and all other coefficients as defined in Ref. [34]. We force

$$\sum_{k=0}^{k_{max}} a_{k,i}=0, \tag{18}$$

to annihilate the $1/r$ prefactor in Eq. (15). This becomes

$$\sum_{k=1}^{k_{max}} a_{k,i}=-1, \tag{19}$$

if we explicitly use $a_{0,i}=1$ (see above). Equation (19) can be fulfilled by setting

$$a_{1,i}=-1-\sum_{k=2}^{k_{max}} a_{k,i}, \tag{20}$$

which fixes the second expansion parameter $a_{k,i}$. Since we want the model potential to behave exactly like the HF-EEIP at the origin, we introduce the parameter η_i,

$$\eta_i=\eta(N,Z,n_i,l_i)=\frac{1}{N-1}W_i^S(0), \tag{21}$$

in analogy to the parameter η in $V^{\mathrm{Green}}(r)$. Then, we construct a third constraint

$$\sum_{k=1}^{k_{max}} k a_{k,i}=-\frac{\eta_i}{\xi_i}, \tag{22}$$

to ensure that $V_i^{\mathrm{GAMP}}(0)=W_i^S(0)$. This is fulfilled if

$$a_{2,i}=-\frac{\eta_i}{\xi_i}+1-\sum_{k=3}^{k_{max}}(k-1)a_{k,i}. \tag{23}$$

After this analysis of the analytical short- and long-range behavior we are able to fix the first three expansion parameters in the GAMP in Eq. (11).

The last constraint can readily be extended to the relativistic DFC case. The only difference is that the two model potentials, $V_i^{P,\mathrm{GAMP}}(r)$ and $V_i^{Q,\mathrm{GAMP}}(r)$, should be applied, since $W_i^P(r)$ and $W_i^Q(r)$ are in general not identical [34]. Therefore, two sets of parameters are used, and especially two constants η_i^P and η_i^Q are necessary to fix the origin behavior of both components separately,

$$\eta_i^P=\eta^P(N,Z,n_i,l_i)=\frac{1}{N-1}W_i^P(0), \tag{24}$$

$$\eta_i^Q=\eta^Q(N,Z,n_i,l_i)=\frac{1}{N-1}W_i^Q(0). \tag{25}$$

Of course, if $\eta_i^P\approx\eta_i^Q$ and also $\xi_i^P\approx\xi_i^Q$ and $a_{k,i}^P\approx a_{k,i}^Q$ within the precision of the GAMP ansatz, we may use a single potential function for $V_i^{P,\mathrm{GAMP}}(r)$ and $V_i^{Q,\mathrm{GAMP}}(r)$. This should be the case for light atoms with $Z\leqslant 50$. The analytical expressions for the origin values of the DFC-EEIPs are similar to those in Eq. (16) and were also derived in Ref. [34].

IV. PARAMETRIZATION OF SHELL-DEPENDENT POTENTIALS

A. Fit expression

To analyze the GAMP ansatz, we determined the parameters of the potential by requiring that the GAMP shall fulfill the HF (DFC) equations. The choice for the fit procedure requires the time-consuming solution of the HF equations. However, this is necessary only for the neutral atoms and some ions. The benefit of the GAMP will be for ions that are not considered in the fit as well as for more sophisticated calculations such as scattering calculations. The homogeneous HF equations (1) discretized on an equidistant grid should be fulfilled at every grid point, provided the exact HF-EEIP $W_i^S(r)$ is used. A model potential can be optimized, such that

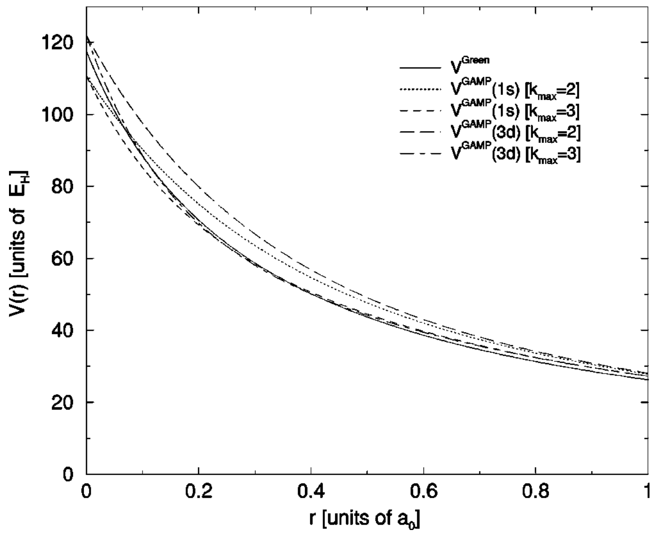

FIG. 1. Nonrelativistic $V_i^{\mathrm{GAMP}}(r)$ for $1s$ and $3d$ shells of Zn ($Z=N=30$) and Green's model potential $V^{\mathrm{Green}}(r)$ for comparison.

$$\sum_p \left[\left(-\frac{1}{2} \frac{d^2}{dr^2}\bigg|_{r=r_p} + \frac{l_i(l_i+1)}{2r_p^2} + V_{\mathrm{nuc}}(r_p) + V_i^{\mathrm{GAMP}}(r_p) - \epsilon_i \right) P_i(r_p) \right]^2 = \min, \tag{26}$$

whereby the radial functions and orbital energies must be given as reference data obtained from numerical HF calculations. The summation is over all grid points. For this fit, the Levenberg-Marquardt optimization algorithm [36] was used, which is a fast method requiring the first derivatives of the function to be minimized with respect to the optimization parameters (see the Appendix for details on the computational methodology). This approach can readily be extended to the relativistic case.

B. Parameters in *GAMP*

As the optimum fit for the potential required many test calculations, we should briefly discuss results from these calculations since they provide a detailed insight into the significance of different terms in the expression of the potential. Furthermore, the final parametrization can only be understood in the light of these results.

Exploratory studies showed that the GAMP in Eq. (11) should be used with at least $k_{max}=3$, i.e., two freely adjustable parameters, ξ_i and $a_{3,i}$, remain. If only one adjustable parameter ($k_{max}=2$) is used, the accuracy of orbital energies, total energies, and radial functions obtained with the model potential is not sufficient. Additionally, if $k_{max}>3$ is chosen, potentials and wave functions are not significantly improved when compared to $k_{max}=3$, which is, of course, due to the fact that exponential functions are introduced which decrease much faster than the first three terms [$\alpha_k=k$ in Eq. (11)]. Figure 1 depicts the model potentials $V_i^{\mathrm{GAMP}}(r)$ for the $1s$ and $3d$ orbitals of Zn for $k_{max}=2$ and $k_{max}=3$. The shell-independent potential $V^{\mathrm{Green}}(r)$ is also displayed. It is evident that $V^{\mathrm{Green}}(r)$ can only reproduce a mean value of the shell-dependent potentials at the origin. Furthermore, at larger distances, the differences between the potentials for the different shells vanish, which is the reason for the good performance of a shell-independent potential. But particularly for the $1s$ orbital, deviations between $V_{1s}^{\mathrm{GAMP}}(r)$ and $V^{\mathrm{Green}}(r)$ become large.

To obtain a shell-dependent potential $V_i^{\mathrm{GAMP}}(r)$ with ansatz Eq. (11), we first determined the values η_i, which fix the origin value of the model potentials. These values were calculated according to Eq. (21), using the analytical expressions for $W_i^S(0)$ given in Ref. [34]. In doing so, we recognized a systematic dependence of η_i on the number of electrons N for neutral atoms. The differences between parameters for two particular shells are almost independent of N. All values are displayed in Fig. 2. Additionally, the parameters ξ_i for neutral atoms are shown in this figure.

Since it is possible to interpolate the GAMP parameters, only very few coefficients for the interpolation polynomials are needed for the complete determination of the GAMP for any system. The following formula can be used to determine parameters $\eta_i(N)$ for all neutral atoms ($Z=N$):

$$\eta_i(N) = b_0^i + b_1\sqrt{N}. \tag{27}$$

The coefficients in this equation are given in Table I. Only one shell-dependent coefficient is introduced per parameter, because the curves in Fig. 2 are almost parallel for all shells and, thus, differ only by a constant. Hence, only a very small number of coefficients remain for the whole periodic table of elements.

We also observe that the parameters ξ_i show a trend very similar to that of η_i (cf. Fig. 2). Therefore, Fig. 2 also plots $\xi_i(N)$ as a function of the values of $\eta_i(N)$ for some shells i of neutral atoms. All curves are perfect straight lines (with an exception at small electron numbers). Hence, the parameters $\xi_i(N)$ for neutral atoms are redundant and can be determined via a relationship of the form

$$\xi_i(N) = k_{0,i} + k_1\eta_i(N), \tag{28}$$

if the values $\eta_i(Z=N)$ are known. The redundancy of $\xi_i(N)$ as expressed in Eq. (28) has the remarkable consequence that the exponential terms of the r dependence of the GAMP are completely determined by the origin behavior of the EEIP. Since the slopes of the curves are almost the same for all shells, only the axis intercept is regarded as shell dependent. These coefficients are also given in Table I. This relationship provides further means to reduce the number of empirical values for the GAMP.

The results obtained with the model potential parametrization so far need to be improved particularly for the valence shells by using an extended GAMP ansatz,

$$V_i^{\mathrm{GAMP}}(r) = \frac{N-1}{r}\left[\sum_{k=0}^{3} a_{k,i}\exp(-k\xi_i r) + br^2\exp(-\xi_i r)\right]. \tag{29}$$

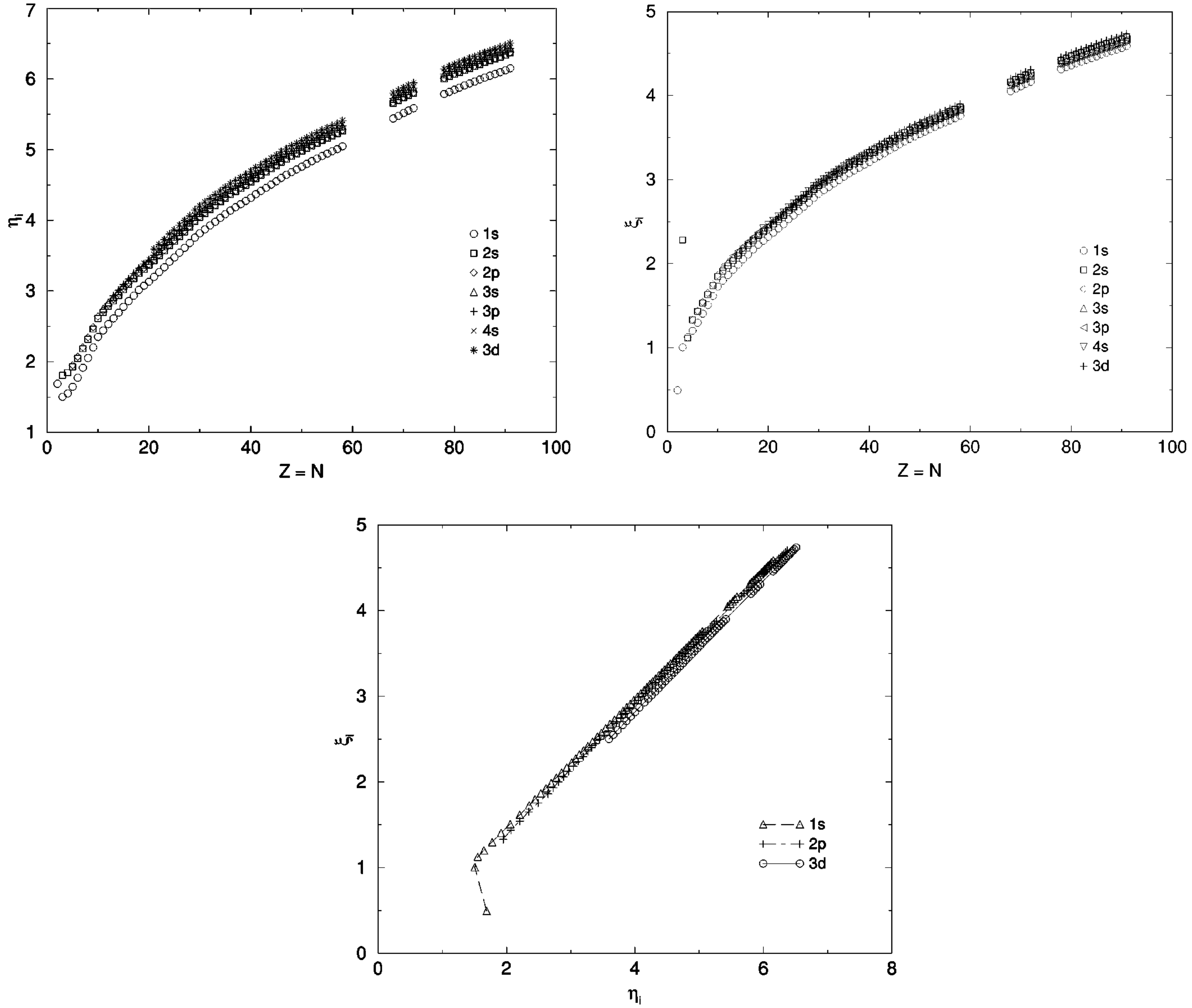

FIG. 2. GAMP parameters $\eta_i(Z,N)$ and $\xi_i(Z=N)$ for shells $1s$ to $3d$ of neutral atoms with $2 \leqslant Z \leqslant 91$, and parameters $\xi_i(Z=N)$ for shells $1s$, $2p$, and $3d$ as functions of $\eta_i(Z=N)$.

The additional term introduced in the potential vanishes at the origin and at long distances, such that neither the short nor the asymptotic behavior of the potential are modified. However, it leads to greater flexibility and better accuracy of the potential.

For the parameters η_i and ξ_i we use the interpolation formulas, Eqs. (27) and (28), as obtained above. The additional parameters $a_{3,i}$ and b are fitted to minimize the differences between the numerical HF (DFC) radial functions and those obtained with the corresponding extended GAMP potentials.[1] These parameters may also be interpolated for many atoms, but this interpolation usually leads to a reduction of the accuracy of wave functions and total energies. Therefore, a list of all parameters in FORTRAN code is deposited as supplementary material[2] or can be obtained from one of the authors (M.R.) to provide all parameters in an easily accessible manner.

C. GAMP parameters for ionic systems

In Eqs. (5) and (6) it was supposed that the parameters for Green's original shell-independent potential show to a good approximation a linear dependence on $[Z-N]$. We find that the GAMP parameters may also be obtained as linear functions of $[Z-N]$ as is demonstrated for Zn-like ions in Fig. 3. Deviations from linearity occur only for the parameters b_i

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[1] This approach was also tested for the adjustment of the parameters ξ_i, but the parameters obtained with this method cannot easily be interpolated, such that we would not be able to derive a compact potential.

[2] See Ref. [40].

TABLE I. Coefficients b_0^i for approximate values of $\eta_i(N)$ according to Eq. (27); the shell-independent coefficient is $b_1 = 0.5930$. Coefficients $k_{0,i}$ for approximate values of $\xi_i(N)$ according to Eq. (28); the shell-independent parameter is $k_1 = 0.7360$.

n_i, l_i	b_0^i	n_i, l_i	b_0^i
$1s$	0.5201	$4d$	0.9361
$2s$	0.7504	$5p$	0.8634
$2p$	0.7607	$6s$	0.8600
$3s$	0.8255	$4f$	0.9823
$3p$	0.8330	$5d$	0.9245
$4s$	0.8569	$6p$	0.8473
$3d$	0.9167	$7s$	0.8330
$4p$	0.8674	$5f$	0.9538
$5s$	0.8704	$6d$	0.8976
n_i, l_i	k_1	n_i, l_i	k_1
$1s$	0.0287	$4d$	-0.0978
$2s$	-0.0309	$5p$	-0.0989
$2p$	-0.0211	$6s$	-0.1019
$3s$	-0.0884	$4f$	-0.1948
$3p$	-0.0838	$5d$	-0.0906
$4s$	-0.0994	$6p$	-0.1011
$3d$	-0.0931	$7s$	-0.1057
$4p$	-0.1005	$6d$	-0.0908
$5s$	-0.0996		

and only for highly charged ions ($[Z-N]>10$). In these cases b_i may be represented by a quadratic function of $[Z-N]$.

This systematic behavior is a general feature for all ions. It is thus possible to calculate the parameters for any ion, if the parameters for the corresponding neutral atom and the slopes of these linear functions are known.

D. Shell-dependent parametrization of Green's potential

The results obtained with the extended GAMP ansatz are in many cases (in particular for heavy atoms with large numbers of electrons) significantly more accurate than the results obtained with the original Green potential. However, *two* shell-dependent parameters remain in the potential which cannot be easily interpolated and must be given explicitly for every atom if the accuracy shall be better than Green's original potential.

Within our approach (as presented in Sec. III A), only *one* freely adjustable parameter per shell remains for the shell-dependent Green potential, since η_i can be fixed in the same manner as it is for $V_i^{\mathrm{GAMP}}(r)$. However, it turns out that using interpolated parameters η_i instead of the exact ones seriously affects the accuracy of wave functions and total electronic energies obtained with this model potential.

The parameters ξ_i were obtained using the fit procedures described in Sec. IV B for the determination of the parameters $a_{3,i}$ and b_i. In contrast to our GAMP, interpolation is not readily possible for these parameters.

The shell-dependent Green potential is significantly improved when compared to Green's original one (in particular for large N). It is in many cases as good as the extended GAMP ansatz. However, neither the parameters ξ_i nor η_i can easily be interpolated without great loss of accuracy. FORTRAN data files are deposited as supplementary material[3] or can be obtained from one of the authors (M.R.) also for the parameters of this shell-dependent Green potential ansatz.

V. VALIDATION OF THE SHELL-DEPENDENT MODEL POTENTIALS

In order to demonstrate the accuracy of the wave functions obtained with the shell-dependent GAMP and shell-dependent Green's model potential, we discuss orbital energies and total electronic energies using the exact HF electron-electron interaction expression but the wave functions calculated with the model potentials. The results for the Zn atom are shown in Table II. It is obvious that optimum results are obtained with our extended GAMP ansatz. The energies calculated with the shell-dependent Green potential are also improved compared to the shell-independent potential although the differences are only small in this case.

In order to investigate the accuracy of the radial wave functions obtained with the extended GAMP ansatz in comparison to those obtained with the original Green potential, the absolute values of the differences between the exact Hartree-Fock radial functions $P_i^{\mathrm{HF}}(r)$ and the radial functions obtained with the model potentials, $P_i^{\mathrm{mod}}(r)$, are shown in Fig. 4 for a core shell ($1s$) and a valence shell ($4s$) of the Zn atom. In both cases, the maximum deviation for Green's original ansatz is more than three times larger than the maximum deviation for the extended GAMP ansatz.

Furthermore, Table III lists $\langle r_i^k\rangle$ and $\langle R^k\rangle$ expectation values ($k=-2,\ldots,+2$) for the Zn atom,

$$\langle r_i^k\rangle = \int_o^\infty dr P_i(r) r^k P_i(r), \tag{30}$$

$$\langle R^k\rangle = \sum_i^{\mathrm{occ}} \langle r_i^k\rangle, \tag{31}$$

in order to demonstrate that also atomic properties, which are calculated with wave functions from the extended GAMP potential, are sufficiently well reproduced and improve on results obtained with Green's original potential. There exist only three exceptions, namely, $\langle r_{3s}^{-2}\rangle$, $\langle r_{3d}\rangle$, and $\langle r_{3d}^2\rangle$, for which the original Green potential yields slightly better results. However, since all other expectation values of these two shells are better reproduced with radial functions from the extended GAMP potential, it does not appear to be worthwhile to improve on these three cases as the accuracy of all other expectation values would be decreased.

The advantages of the shell-dependent model potentials are more impressive for neutral atoms with many electrons.

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[3] See Ref. [40].

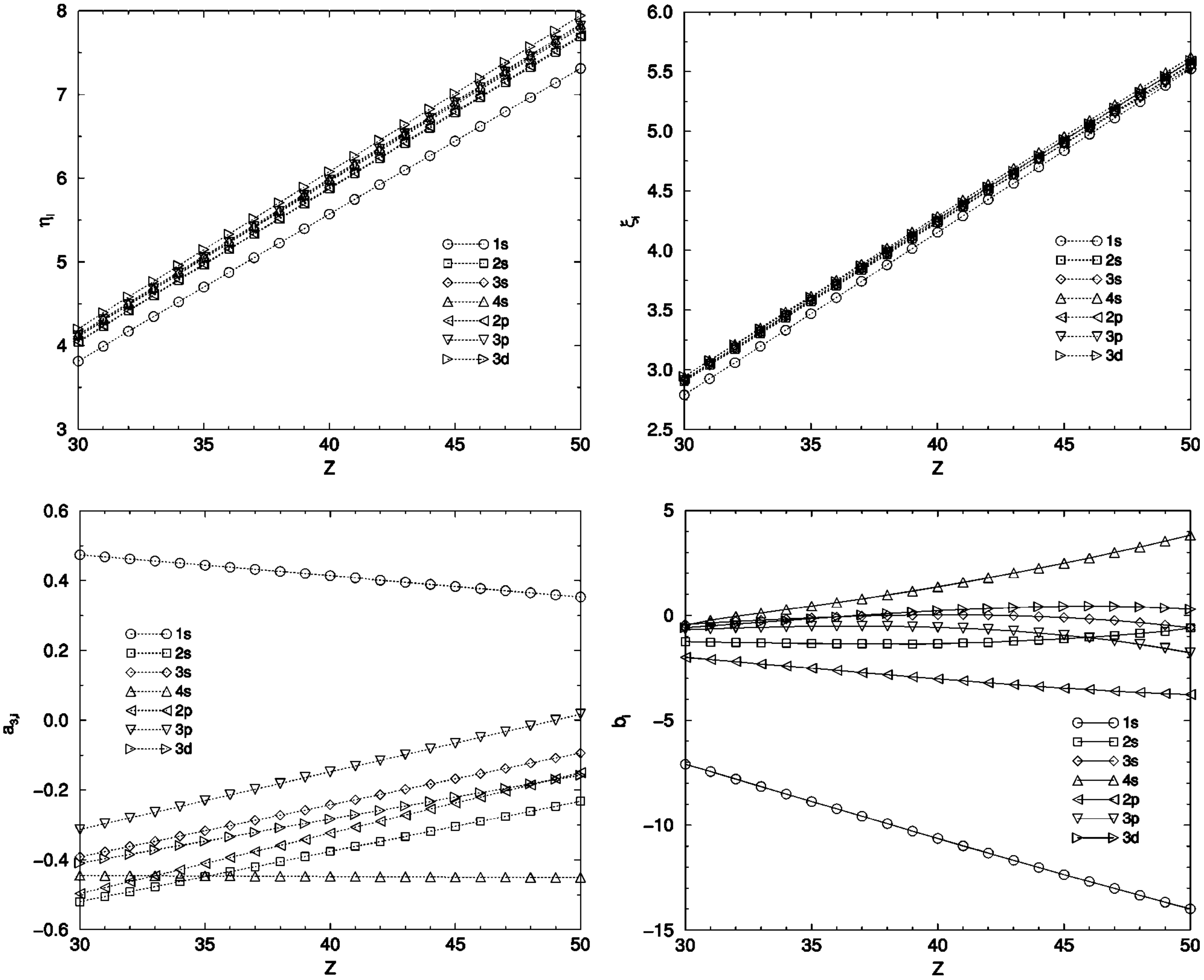

FIG. 3. Values of the GAMP parameters $\eta_i(Z,N)$, $\xi_i(Z,N)$, $a_{3,i}(Z,N)$, and $b_i(Z,N)$ for shells $1s$ to $3d$ of Zn-like ions ($N=30$).

Table IV gives the total electronic energies for atoms with $80 \leqslant N \leqslant 90$. While the accuracy of the total energies is comparable for both shell-dependent model potentials, the differences between the shell-independent Green potential and the exact Hartree-Fock energies are larger.

VI. RELATIVISTIC EFFECTS ON GAMP PARAMETERS

A relativistic test parametrization has been performed with our GAMP ansatz using a pointlike nucleus for $V_{\mathrm{nuc}}(r)$. Since in this case, $W_i^P(0)$ and $W_i^Q(0)$ in Eq. (2) are only well

TABLE II. Orbital energies ϵ_i and total electronic energies $\langle E \rangle$ of Zn ($Z=N=30$), obtained using different model potentials. HF: exact Hartree-Fock energies; Green: Green's model potential with the original, shell-independent parametrization; Green, sd: Green's model potential with the shell-dependent parametrization derived in this work; ext. GAMP: extended GAMP ansatz in Eq. (29). Numbers in square brackets denote powers of 10.

n,l	ϵ^{HF}	$\epsilon^{\mathrm{Green}}$	$\epsilon^{\mathrm{Green},sd}$	$\epsilon^{\mathrm{ext.\ GAMP}}$
$1s$	−3.5330454[+2]	−3.5299653[+2]	−3.5329532[+2]	−3.5338200[+2]
$2s$	−4.4361720[+1]	−4.4253656[+1]	−4.4301302[+1]	−4.4416499[+1]
$3s$	−5.6378156[+0]	−5.5340377[+0]	−5.5311290[+0]	−5.6670789[+0]
$4s$	−2.9250714[−1]	−2.4885151[−1]	−2.8052838[−1]	−3.0098443[−1]
$2p$	−3.8924839[+1]	−3.8807749[+1]	−3.8875229[+1]	−3.8983615[+1]
$3p$	−3.8393732[+0]	−3.7372392[+0]	−3.7405494[+0]	−3.8692636[+0]
$3d$	−7.8253672[−1]	−6.8206128[−1]	−6.9169695[−1]	−8.1124037[−1]
$\langle E \rangle$	−1.7778481[+3]	−1.7777338[+3]	−1.7777625[+3]	−1.7778260[+3]

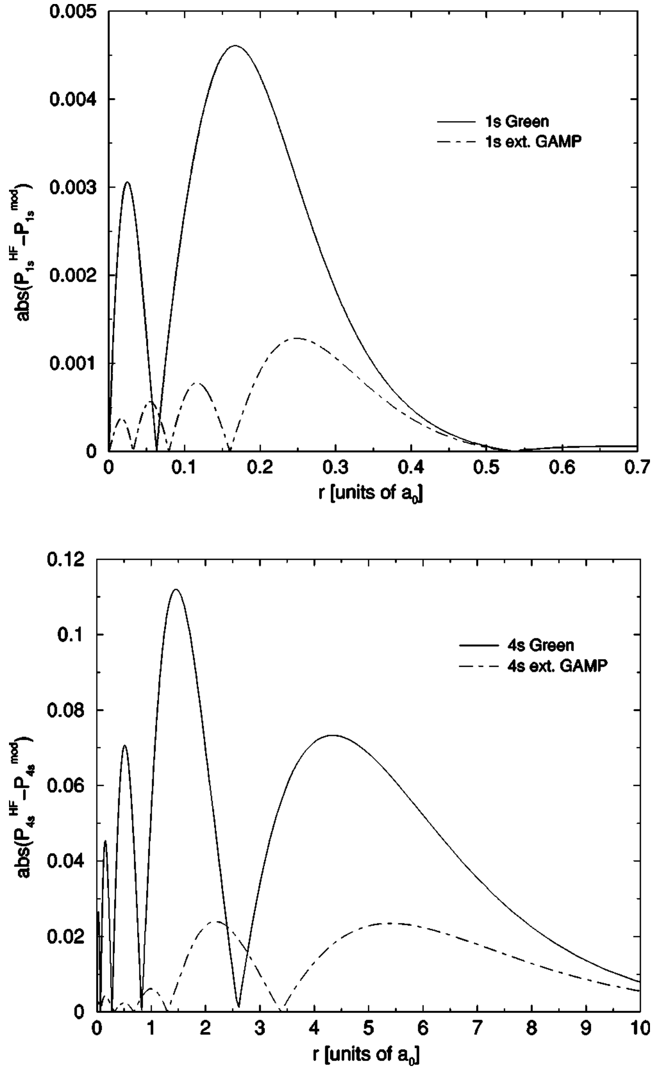

FIG. 4. Absolute values of the differences of Hartree-Fock radial functions (P_i^{HF}) and radial functions obtained using Green's model potential ansatz with the original, shell-independent parametrization and using our extended GAMP ansatz, resp., for the Zn atom. Top: core shell $1s$; bottom: valence shell $4s$. Note the different scales.

defined for $|\kappa_i|=1$, it is necessary to obtain approximate nonsingular values of these potentials at the origin in order to use Eqs. (24) and (25), since such DFC-EEIPs occur which behave like r^{β} with $-1<\beta<0$ and are, thus, singular [34]. Usually, $|\beta|\ll 1$ in these cases, such that the singularities are limited to very small values of r. We approximately set $\beta := 0$, which yields a regular behavior of the DFC-EEIPs at the origin.

Since we do not aim at an extension of our GAMP parameter set, we investigate the change of the nonrelativistic GAMP parameters, if Dirac one-electron operators are used instead of Schrödinger-type operators. As an example, the relative deviations between nonrelativistic and relativistic η_i parameters, i.e., the relative relativistic effects on the nonrelativistic GAMP parameters, are shown for the large component of the s shells $P_{ns}^{DFC}(r)$ in Fig. 5.

To elucidate the relativistic effect on the electron-electron interaction model potentials in greater detail extended further studies within the four-component framework are needed as the parameters $a_{3,i}$ and b_i need to be determined accurately for relativistically modified parameters η_i. However, since a large contribution to the relativistic energy lowering is due to kinematic effects rather than due to relativistic effects on the electron-electron interaction, the shell-dependent parametrization of the nonrelativistic ansatz may be used as a good first approximation: As can be seen from Fig. 5, the relativistic effect on η_i is only about 5% for $Z=60$.

VII. CONCLUSION

To summarize we note that an improvement of analytical local model potentials can be achieved by a shell-dependent parametrization. The reason for this can be traced back to the shell dependence of the origin behavior of the HF- and DF-EEIPs as shown in Ref. [34]. In particular, the calculation of a $1s$ orbital by a shell-independent potential would cause difficulties.

The disadvantage of a large number of freely adjustable parameters, which result from the shell-dependence, can be overcome in parts by the particular ansatz that we chose for the GAMP. The analytical expressions from the origin behavior of the HF-EEIPs, which fix the parameters η_i, cannot readily be calculated for all atoms as they are of great complexity. However, they can easily be interpolated throughout the whole periodic table, which holds also for the parameter ξ_i of the GAMP.

In addition, we presented a shell-dependent parametrization for the original model potential ansatz by Green. In case of this ansatz, neither η_i nor ξ_i can be interpolated if an accuracy in wave functions and total electronic energies comparable to the extended GAMP potential shall be obtained. This implies for both potentials, GAMP and Green, that two shell-dependent parameters remain which cannot be given in terms of interpolation formulas but have to be specified explicitly. It is not possible to obtain results of sufficient accuracy with less than two shell-dependent parameters, independent of the ansatz chosen for the potential.

We refrain from deriving l-dependent parametrization of the model potentials because the accuracy per shell can only be maintained if the parameters are taken as they are. Moreover, it is only the parameters for $1s$ shells which deviate largely from the rest.

Particularly, for $N \geqslant 50$, we recommend to use our shell-dependent model potentials rather than a shell-independent one as these yield a higher accuracy for wave functions and thus also for the prediction of atomic properties. Furthermore, the parameters for ions can easily be obtained from the parameters of the corresponding neutral atoms for our extended GAMP potential.

Within this work it was possible to clarify those aspects of local electron-electron interaction model potentials of simple analytical form which have not yet been covered in the extensive studies by Green and co-workers. Future work may now focus on a detailed investigation of relativistic effects in the potential parameters for heavy and superheavy atoms, for

TABLE III. $\langle r_i^k \rangle$ and $\langle R^k \rangle$ expectation values ($k=-2,\dots,+2$) of Zn ($Z=N=30$) obtained using different model potentials. HF: exact HF values; Green: Green's model potential with the original, shell-independent parametrization; ext. GAMP: extended GAMP ansatz. Numbers in square brackets denote powers of 10.

n,l	$\langle r_i^k \rangle$	HF	Green	ext. GAMP
$1s$	$\langle 1/r^2 \rangle$	1.75107182[+3]	1.75369[+3]	1.75135[+3]
	$\langle 1/r \rangle$	2.95120538[+1]	2.95410[+1]	2.95137[+1]
	$\langle r \rangle$	5.10849147[−2]	5.10033[−2]	5.10843[−2]
	$\langle r^2 \rangle$	3.49712056[−3]	3.48288[−3]	3.49665[−3]
$2s$	$\langle 1/r^2 \rangle$	1.70816767[+2]	1.70147[+2]	1.70658[+2]
	$\langle 1/r \rangle$	6.46708097[+0]	6.45320[+0]	6.46550[+0]
	$\langle r \rangle$	2.28772893[−1]	2.29308[−1]	2.28583[−1]
	$\langle r^2 \rangle$	6.16716287[−2]	6.20145[−2]	6.14810[−2]
$3s$	$\langle 1/r^2 \rangle$	2.53293809[+1]	2.53063[+1]	2.56461[+1]
	$\langle 1/r \rangle$	2.04010083[+0]	2.03133[+0]	2.04190[+0]
	$\langle r \rangle$	6.90586511[−1]	6.94073[−1]	6.92826[−1]
	$\langle r^2 \rangle$	5.50224362[−1]	5.55248[−1]	5.54680[−1]
$4s$	$\langle 1/r^2 \rangle$	1.15541037[+0]	1.93508[+0]	1.21107[+0]
	$\langle 1/r \rangle$	4.41877240[−1]	5.23093[−1]	4.34997[−1]
	$\langle r \rangle$	2.89773844[+0]	2.52365[+0]	3.00253[+0]
	$\langle r^2 \rangle$	9.86940953[+0]	7.48766[+0]	10.7243[+0]
$2p$	$\langle 1/r^2 \rangle$	5.59654388[+1]	5.70407[+1]	5.60212[+1]
	$\langle 1/r \rangle$	6.40175601[+0]	6.45740[+0]	6.40305[+1]
	$\langle r \rangle$	1.99513736[−1]	1.98211[−1]	1.99419[−1]
	$\langle r^2 \rangle$	4.87287313[−2]	4.81849[−2]	4.86090[−2]
$3p$	$\langle 1/r^2 \rangle$	7.91488187[+0]	7.98385[+0]	7.97394[+0]
	$\langle 1/r \rangle$	1.90442292[+1]	1.90856[+1]	1.90489[+0]
	$\langle r \rangle$	7.19787236[−1]	7.17307[−1]	7.20189[−1]
	$\langle r^2 \rangle$	6.11174072[−1]	6.05118[−1]	6.10922[−1]
$3d$	$\langle 1/r^2 \rangle$	3.20258439[+0]	3.14336[+0]	3.19954[+0]
	$\langle 1/r \rangle$	1.53053853[+0]	1.51863[+0]	1.52981[+0]
	$\langle r \rangle$	8.74871617[−1]	8.74919[−1]	8.81027[−1]
	$\langle r^2 \rangle$	1.00500842[+0]	0.99588[+0]	1.03807[+0]
Total	$\langle 1/R^2 \rangle$	4.31205453[+3]	4.32373[+3]	4.31369[+3]
	$\langle 1/R \rangle$	1.42064685[+2]	1.42479[+2]	1.42058[+2]
	$\langle R \rangle$	2.20008875[+1]	2.12384[+1]	2.22780[+1]
	$\langle R^2 \rangle$	3.49791064[+1]	3.00954[+1]	3.70258[+1]

TABLE IV. Total electronic energies $\langle E \rangle$ for neutral atoms with $80 \leqslant Z \leqslant 90$, obtained using different model potentials. HF: exact HF energies; Green: Green's model potential with the original, shell-independent parametrization; Green,*sd*: Green's model potential with the shell-dependent parametrization derived in this work; ext. GAMP: extended GAMP ansatz in Eq. (29).

$N=Z$	$\langle E \rangle^{\mathrm{HF}}$	$\langle E \rangle^{\mathrm{Green}}$	$\langle E \rangle^{\mathrm{Green},sd}$	$\langle E \rangle^{\mathrm{ext.\ GAMP}}$
80	−18408.9915	−18395.8598	−18406.8045	−18407.2005
81	−18961.8248	−18949.5815	−18959.6704	−18960.0383
82	−19524.0080	−19512.6066	−19521.8774	−19522.1890
83	−20095.5864	−20085.0237	−20093.4821	−20093.6909
84	−20676.5009	−20666.6235	−20674.4245	−20674.5229
85	−21266.8817	−21257.6845	−21264.8319	−21264.7945
86	−21866.7722	−21858.2225	−21864.7465	−21864.5561
87	−22475.8587	−22468.6019	−22473.8804	−22473.4620
88	−23094.3037	−23088.2216	−23092.3661	−23091.7326
89	−23722.1921	−23716.7724	−23720.2883	−23719.1821
90	−24359.6224	−24354.8138	−24357.7474	−24356.0491

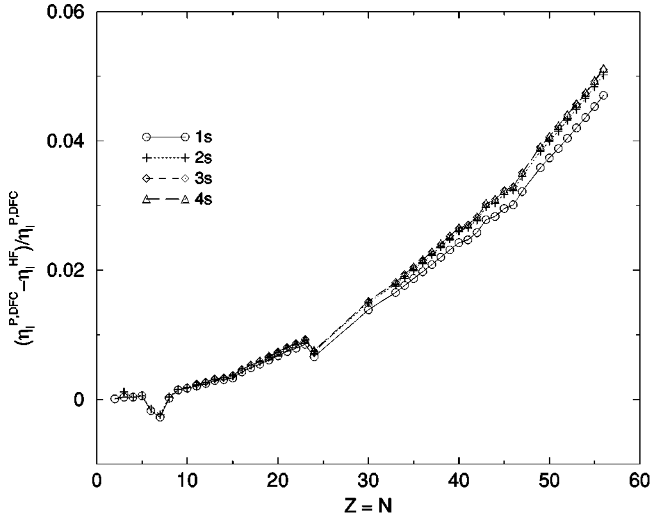

FIG. 5. Relative deviations of the relativistic and nonrelativistic GAMP parameters $(\eta_i^{P,DFC}-\eta_i^{HF})/\eta_i^{P,DFC}$ for *s* shells of neutral atoms.

which the benefit of the use of a model potential is large because of the increasing number of electrons.

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APPENDIX: NUMERICAL METHODS

All radial functions, energy eigenvalues and other reference data were obtained with the fully numerical MCSCF atomic structure programs ATOM [21] for HF calculations and ADRIEN [22] for DFC calculations. The implemented numerical discretization schemes and solution methods are described elsewhere [21,22,37,38]. Hartree atomic units are used throughout this article, i.e., the numerical values of the elementary charge, $4\pi\epsilon_0$, $\hbar$, and the mass of an electron are chosen to be equal to one. Accordingly, energies are measured in units of $E_H=e^2/(4\pi\epsilon_0 a_0)$, i.e., in hartree and distances in units of $a_0=4\pi\epsilon_0\hbar/(m_e e^2)$, i.e., in bohr. For the relativistic calculations, the value for the speed of light, $c=137.035\,989\,5$, was taken from Ref. [39]. All results were obtained with 2000 inner grid points.

For fitting the parameters, we used standard optimization routines for Levenberg-Marquardt and Simplex minimization [36]. All further calculations necessary for the optimization were done utilizing the same numerical techniques as in the underlying atomic structure packages (see references given above).

Because of particular features of the configuration-state-function handling in our atomic structure programs we did not perform calculations for atoms with $50\leqslant Z\leqslant 67$ and $73\leqslant Z\leqslant 77$. However, this does not affect our results since the parameters can be interpolated quite well.

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