Analysis of the asymptotic and short-range behavior of quasilocal Hartree-Fock and Dirac-Fock-Coulomb electron-electron interaction potentials

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The analytic origin behavior of Hartree-Fock and Dirac-Fock-Coulomb electron-electron interaction potentials is derived. This yields explicit expressions, which depend on $\langle 1/r^n \rangle$ matrix elements. The direct part of the electron-electron interaction including the self-interaction is equal for all shells. If the self-interaction is subtracted the Coulomb part will become shell dependent. Additional shell dependence of the origin behavior originates from the true exchange-interaction terms. For the Dirac-Fock-Coulomb operator we find singular behavior for non *s* shells, if a Coulomb-type electron-nucleus potential is used, while it is nonsingular for *s* shells. For all shells in case of finite nuclear models, the electron-electron interaction potentials are nonsingular at the origin. A comparison of potentials for the small and large component of the relativistic radial spinor shows that they are equal in the long-range limit, while this is not true, in general, at the origin. The analytic results presented are tested by comparing them to numerical results obtained for the zinc atom.

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I. INTRODUCTION

The Hartree-Fock (HF) method is a well-known approach for electronic-structure calculations of atoms. Its relativistic analog, the Dirac-Hartree-Fock or Dirac-Fock theory, uses the relativistic Dirac Hamiltonian as the one-electron operator. The exact relativistic many-particle Hamiltonian is not known. Therefore, simple Coulomb-type operators are usually used to describe the electron-electron interaction. We will denote this approach as the Dirac-Fock-Coulomb (DFC) method. Both the HF and DFC methods are independent-particle theories and therefore do not include correlation effects.

The most computer-time consuming part in the HF and DFC calculations concerns the calculation of electron-electron-interaction matrix elements. Since all orbitals enter the electron-electron interaction potentials (EEIPs) in the HF and DFC equations, these equations can only be solved iteratively in a self-consistent-field procedure. Another difficulty is that the EEIPs contain nonlocal exchange-interaction terms, so that inhomogeneous differential equations must be solved. Many attempts have been made to simplify these potentials by replacing them by local potentials (cf. e.g., [1–3]), so that homogeneous equations are obtained, which are computationally less demanding. This is the case in density-functional theory [4,5]. Another example can be found in the optimized-potential method by Talman and Shadwick [6]. The optimized-potential method determines a local potential such that the expectation value of the Hamiltonian is minimized, and it has been regarded as the exact Kohn-Sham exchange potential for atoms [7]. Further simplification can be achieved by analytical independent-particle model potentials (cf. e.g., [8–11]), which are simple analytical expressions and replace the two-electron integrals in the HF and DFC equations. For these approaches, analytically derived properties of EEIPs in the HF and DFC models are very useful (compare, for instance, the search for an exchange potential that decreases as $1/r$ [28]). While the long-range asymptotic behavior is known, the short-range behavior has not yet been analyzed in detail.

Although it can be seen from early work by Hartree [1] that the EEIPs within HF theory are different for different shells at the origin, shell-independent EEIPs are used in Kohn-Sham theory and in the optimized-potential method. Explicit analytical expressions for the short-range behavior of the nonrelativistic and relativistic EEIPs have not yet been given. Such an analysis of the short-range behavior of the electron-electron interaction terms is carried out here. It is performed for nonrelativistic Hartree-Fock potentials as well as for Dirac-Fock-Coulomb potentials.

Information on analytically determined shell-dependent properties of these potentials may be of importance for the development of Kohn-Sham effective exchange potentials (compare, for instance, [5,12–14]), effective core potentials (see [15] for their introduction into the self-consistent-field equations for atoms), and analytical independent-particle model potentials [8–11].

The paper is organized as follows. In Sec. II, a short summary of the HF and DFC notation is given and general expressions for the EEIPs are derived. Section III presents analytical expressions for the EEIPs at the origin in terms of $\langle 1/r^n \rangle$ matrix elements, while Sec. IV briefly deals with the asymptotic behavior. Graphical representation of numerical calculated EEIPs in Sec. V confirms the analysis presented.

II. HARTREE-FOCK AND DIRAC-FOCK-COULOMB THEORY FOR ATOMS

To clarify the notation used, we recall essential elements of the HF and DFC theory. Detailed presentations of these

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theories may be found in [16–19]. Since our analysis concerns electronic ground states in atoms, the central-field approximation is adopted. 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 1. Accordingly, energies are measured in units of $E_h = e^2/(4\pi\epsilon_0 a_0)$, i.e., in hartrees and distances are measured in units of $a_0 = 4\pi\epsilon_0\hbar/(m_e e^2)$, i.e., in bohrs.

A. Hamiltonian and one-electron functions

The many-electron Hamiltonian in the HF and DFC theory can be written as

$$H = \sum_{i=1}^{N} h(i) + \frac{1}{2}\sum_{i\neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{1}$$

where $h(i)$ is defined as

$$h(i) = \begin{cases} -\frac{1}{2}\mathbf{p}_i^2 + V_{\mathrm{nuc}}(r_i), & \text{HF theory} \\ c\boldsymbol{\alpha}(i)\cdot\mathbf{p} + c^2\beta(i) + V_{\mathrm{nuc}}(r_i), & \text{DFC theory.} \end{cases} \tag{2}$$

These equations are given in the standard representation, i.e., $\mathbf{p}_i = -i\boldsymbol{\nabla}_i$ is the momentum operator, $\boldsymbol{\alpha}$ is a three-vector of 4×4 matrices containing Pauli spin matrices, and β is a 4×4 diagonal matrix [19]. N is the total number of electrons and $V_{\mathrm{nuc}}(r)$ is the electron-nucleus interaction potential,

$$V_{\mathrm{nuc}}(r) = \begin{cases} -\frac{Z}{r}, & \text{point nucleus,} \\ \text{model potentials,} & \text{finite nucleus.} \end{cases} \tag{3}$$

A comprehensive overview of different finite-nucleus models is given in [20]. The ansatz for a one-electron function within the central-field approximation is in the HF formalism a spin orbital,

$$\psi_i^{HF} = \psi_{n_i l_i m_{l,i} m_{s,i}} = \frac{P_{n_i l_i}(r)}{r} Y_{l_i m_{l,i}}(\theta,\phi)\chi_{m_{s,i}}(\sigma), \tag{4}$$

and a spinor,

$$\psi_i^{DFC} = \psi_{n_i \kappa_i m_{j,i}} = \frac{1}{r}\begin{pmatrix} P_{n_i\kappa_i}(r)\chi_{\kappa_i m_{j,i}}(\theta,\phi) \\ \mathrm{i}Q_{n_i\kappa_i}(r)\chi_{-\kappa_i m_{j,i}}(\theta,\phi) \end{pmatrix} \tag{5}$$

in the DFC formalism. $P_{n_i l_i}(r)$, $P_{n_i\kappa_i}(r)$ (the large component), and $Q_{n_i\kappa_i}(r)$ (the small component) are radial functions. In the nonrelativistic formalism, $Y_{l_i m_{l,i}}$ are spherical harmonics and $\chi_{m_{s,i}}(\sigma)$ are spin functions, while in the relativistic analog $\chi_{\kappa_i m_{j,i}}$ are two-component spherical spinors, where the spherical harmonics have been coupled with the spin function. Here we have used the central-field approximation and the equivalence restriction, i.e., we use the same radial functions for spin orbitals belonging to the same shell. Shells are defined by pairs of quantum numbers: in the nonrelativistic case by $\{n_i, l_i\} = i$ and in the relativistic case by $\{n_i, \kappa_i\} = i$.

B. Total electronic-energy expectation value

The total energy for closed-shell atoms after integration over all angular and spin coordinates is given by

$$\langle E\rangle = \sum_i D_i h_{ii} + \frac{1}{2}\sum_{ij} D_i D_j \Big[\langle\rho_{ii}U_{jj0}\rangle - \frac{1}{2}\sum_\nu A_{ij\nu}\langle\rho_{ij}U_{ji\nu}\rangle\Big]. \tag{6}$$

In order to treat nonrelativistic and relativistic approaches on the same footing, we introduced

$$h_{ii} = \begin{cases} \langle P_i(r)|h_S(r)|P_i(r)\rangle, & \text{HF} \\ \langle (P_i(r),Q_i(r))|h_D(r)|(P_i(r),Q_i(r))\rangle, & \text{DFC,} \end{cases} \tag{7}$$

and the radial density

$$\rho_{ij}(r) = \begin{cases} P_i(r)P_j(r), & \text{HF} \\ P_i(r)P_j(r) + Q_i(r)Q_j(r), & \text{DFC.} \end{cases} \tag{8}$$

The one-electron operators $h_{S,D}(r)$ in h_{ii} are the radial Schrödinger and Dirac operators, respectively,

$$h_{S,D}(r) = \begin{cases} h_S(r) = \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{2r^2} + V_{\mathrm{nuc}}(r)\right], & \text{HF} \\ h_D(r) = \begin{bmatrix} V_{\mathrm{nuc}}(r) & A_i^\dagger(r) \\ A_i(r) & V_{\mathrm{nuc}}(r) - 2c^2 \end{bmatrix}, & \text{DFC,} \end{cases} \tag{9}$$

with

$$A_i(r) = c\left(\frac{d}{dr} + \frac{\kappa_i}{r}\right) \quad \text{and} \quad A_i^\dagger = -c\left(\frac{d}{dr} - \frac{\kappa_i}{r}\right). \tag{10}$$

Further, we utilized the Laplace expansion for the operator $1/(|\mathbf{r}_i - \mathbf{r}_j|)$ (cf., e.g., [21]) leading to potential functions

$$U_{ij\nu}(r_1) = \frac{1}{r_1^{\nu+1}}\int_0^{r_1} dr_2[\rho_{ij}(r_2)r_2^\nu] + r_1^\nu\int_{r_1}^\infty dr_2[\rho_{ij}(r_2)/r_2^{\nu+1}], \tag{11}$$

which are part of the two-electron integrals

$$\langle\rho_{kl}U_{ij\nu}\rangle = \int_0^\infty dr_1\rho_{kl}(r_1)U_{ij\nu}(r_1). \tag{12}$$

In the case of HF theory, the sum over ν runs from $|l_i - l_j|$ to $l_i + l_j$, with $\nu + l_i + l_j$ even. In the relativistic DFC frame-

work, the summation is for all ν from $|j_i - j_j|$ to $j_i + j_j$, with $\nu + j_i + j_j$ odd if $\mathrm{sgn}(\kappa_i) = \mathrm{sgn}(\kappa_j)$, and $\nu + j_i + j_j$ even if $\mathrm{sgn}(\kappa_i) \neq \mathrm{sgn}(\kappa_j)$.

The symmetry coefficients are

$$A_{ij\nu}^{HF} = \begin{pmatrix} l_i & \nu & l_j \\ 0 & 0 & 0 \end{pmatrix}^2, \tag{13}$$

$$A_{ij\nu}^{DFC} = 2\begin{pmatrix} j_i & \nu & j_j \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}^2. \tag{14}$$

Since we are dealing with closed-shell atoms, the occupation numbers may be written as

$$D_i = \begin{cases} 4l_i + 2, & \text{HF} \\ 2j_i + 1, & \text{DFC.} \end{cases} \tag{15}$$

C. Self-consistent-field equations

Variation of the HF total electronic-energy expectation value with respect to the orbitals yields the radial HF equations [1,22], which we may write here as homogeneous differential equations

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{2r^2} + V_{\mathrm{nuc}}(r) + W_i^S(r) - \epsilon_i \right) P_i(r) = 0, \tag{16}$$

where we introduced the *quasilocal* HF electron-electron interaction potential

$$\begin{aligned} W_i^S(r) &= \sum_j D_j \left[U_{jj0}(r) - \frac{1}{2}\sum_\nu A_{ij\nu}^{HF} U_{ji\nu}(r) P_j(r)/P_i(r) \right] \\ &= V_i(r) + \frac{X_i^S(r)}{P_i(r)}, \end{aligned} \tag{17}$$

whereby the functions $V_i(r)$ and $X_i^S(r)$ are being dicussed in detail in the sequel (superscript S indicates the nonrelativistic Hartree-Fock approach based on the Schrödinger one-electron operator). The HF equations are only artificially homogeneous (and therefore the HF EEIPs are quasilocal), since inhomogeneities arise from the j-shell contributions through $P_j(r)$. Analogously to the above HF treatment, we obtain for the relativistic DFC equations

$$\begin{pmatrix} V_{\mathrm{nuc}}(r) + W_i^P(r) - \epsilon_i & A_i^\dagger(r) \\ A_i(r) & V_{\mathrm{nuc}}(r) + W_i^Q(r) - 2c^2 - \epsilon_i \end{pmatrix} \times \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \tag{18}$$

with the quasilocal DFC EEIPs

$$\begin{aligned} W_i^P(r) &= \sum_j D_j \left[U_{jj0}(r) - \frac{1}{2}\sum_\nu A_{ij\nu}^{DFC} U_{ji\nu}(r) P_j(r)/P_i(r) \right] \\ &= V_i(r) + \frac{X_i^P(r)}{P_i(r)}, \end{aligned} \tag{19}$$

$$\begin{aligned} W_i^Q(r) &= \sum_j D_j \left[U_{jj0}(r) - \frac{1}{2}\sum_\nu A_{ij\nu}^{DFC} U_{ji\nu}(r) Q_j(r)/Q_i(r) \right] \\ &= V_i(r) + \frac{X_i^Q(r)}{Q_i(r)}, \end{aligned} \tag{20}$$

whereby the functions $V_i(r)$ and $X_i^{(P,Q)}(r)$ and their nonrelativistic analogs will be analyzed in the following. These quasilocal self-consistent-field potentials $W_i^{(S,P,Q)}(r)$ contain two different parts, $V_i(r)$ and $X_i^{(S,P,Q)}(r)$. For the homogeneous part, $V_i(r)$, which represents the Coulomb interaction and the correction for the self-interaction, we get

$$V_i(r) = \sum_j D_j U_{jj0}(r) - \frac{1}{2} D_i \sum_\nu A_{ii\nu} U_{ii\nu}(r) \tag{21}$$

for both, the HF and DFC potentials. The inhomogeneous part, which originates from the exchange interaction only, is in the nonrelativistic HF framework,

$$X_i^S(r) = -\frac{1}{2}\sum_{j,j\neq i} D_j \sum_\nu A_{ij\nu}^{HF} U_{ji\nu}(r) P_j(r), \tag{22}$$

while we obtain in the relativistic case

$$X_i^P(r) = -\frac{1}{2}\sum_{j,j\neq i} D_j \sum_\nu A_{ij\nu}^{DFC} U_{ji\nu}(r) P_j(r), \tag{23}$$

$$X_i^Q(r) = -\frac{1}{2}\sum_{j,j\neq i} D_j \sum_\nu A_{ij\nu}^{DFC} U_{ji\nu}(r) Q_j(r). \tag{24}$$

III. SHORT-RANGE BEHAVIOR OF HF AND DFC EEIPS

A. Closed-shell atoms

To analyze the short-range behavior of the potentials, we make use of the series expansion of the HF radial functions,

$$P_i^{HF}(r) = r^{l_i+1} \sum_{k=0}^{\infty} a_{k,i}^{HF} r^k, \tag{25}$$

and of the DF radial functions,

$$P_i^{DFC}(r) = r^{\alpha_i} \sum_{k=0}^{\infty} a_{k,i}^{DFC} r^k, \quad Q_i(r) = r^{\alpha_i} \sum_{m=0}^{\infty} b_{m,i} r^m, \tag{26}$$

about the origin. According to Eqs. (21)–(24), we must

evaluate the behavior of the potential functions $U_{ij\nu}(r)$,[1]

$$\lim_{r_1\to 0} U_{ij\nu}^{HF}(r_1)=\lim_{r_1\to 0}\left[r_1^{k-1}\left(\frac{a_{0,i}^{HF}a_{0,j}^{HF}}{\nu+k}-\frac{a_{0,i}^{HF}a_{0,j}^{HF}}{k-\nu-1}\right)+r_1^{\nu}\left\langle\frac{\rho_{ij}^{HF}(r_2)}{r_2^{\nu+1}}\right\rangle+O(r_1^k)\right], \tag{27}$$

with $k=3+l_i+l_j\geqslant 3$, and similarly

$$\lim_{r_1\to 0} U_{ij\nu}^{DFC}(r_1)=\lim_{r_1\to 0}\left[r_1^{m-1}(a_{0,i}^{DFC}a_{0,j}^{DFC}+b_{0,i}b_{0,j})\left(\frac{1}{\nu+m}-\frac{1}{m-\nu-1}\right)+r_1^{\nu}\left\langle\frac{\rho_{ij}^{DFC}(r_2)}{r_2^{\nu+1}}\right\rangle+O(r_1^m)\right], \tag{28}$$

with $m=1+\alpha_i+\alpha_j\geqslant 1$. Here we used the power-series expansions, Eqs. (25) and (26), respectively. In both equations the first term vanishes at the origin, and from the second term we get contributions only if $\nu=0$. Therefore we obtain the result

$$\lim_{r_1\to 0} U_{ij\nu}(r_1)=\begin{cases}0, & \nu\neq 0\\ \langle\rho_{ij}/r_2\rangle, & \nu=0,\end{cases} \tag{29}$$

valid for the HF and DFC potential functions.

Since the constraint $\nu=0$ in Eq. (29) can only be fulfilled if $l_i=l_j$ or $j_i=j_j$, respectively, and the symmetry coefficients are then given as (cf. e.g., [23])

$$A_{ii0}=2/D_i, \tag{30}$$

the value of the homogeneous part of the HF EEIPs and DFC EEIPs at the origin is

$$\lim_{r\to 0} V_i(r)=\sum_j D_j\langle\rho_{jj}/r\rangle-\langle\rho_{ii}/r\rangle. \tag{31}$$

However, the short-range behavior of the inhomogeneous part $X_i^R(r)/R_i(r)$ (with R being $\{S,P,Q\}$ and R_i being the corresponding radial function) of the EEIPs is different in nonrelativistic and relativistic theory due to the exponents in the series expansions of the radial functions, Eqs. (25) and (26). This difference has its origin in the structure of the differential equations (16), which are of second order, and Eqs. (18), which are coupled first-order differential equations. The way in which the structure of the differential equations affects the exponents in the radial functions' series expansions is explicated, for instance, in Refs. [15] and [24]. In the case of the DFC theory it turns out that these exponents additionally depend on the type of model used for the nucleus, i.e., point nucleus or finite nucleus. In contrast to the DFC theory, the exponents are independent of the electron-nucleus interaction model within the HF theory. The analysis of $\lim_{r\to 0}[X_i^R(r)/R_i(r)]$ is lengthy but straightforward and is given in the Appendix. If the homogeneous part $V_i(r)$ of the total HF EEIP is added to the inhomogeneous term $X_i^S(r)/P_i(r)$, whose short-range behavior is given in Eq. (A3) in the Appendix, we obtain

$$W_i^S(0)=\lim_{r\to 0}[V_i(r)+X_i^S(r)/P_i(r)] \tag{32}$$

$$=\langle 1/R\rangle-\langle\rho_{ii}^{HF}/r\rangle-\frac{1}{2}\sum_{j;\{j\neq i,l_j\leqslant l_i\}} D_j A_{ij(l_i-l_j)}^{HF}\times\langle\rho_{ij}^{HF}/r^{l_i-l_j+1}\rangle\frac{a_{0,j}^{HF}}{a_{0,i}^{HF}}, \tag{33}$$

where we introduced the expectation value

$$\langle 1/R\rangle=\sum_i D_i\langle\rho_{ii}/r\rangle, \tag{34}$$

which is the shell-independent part of $W_i^S(0)$ originating solely from the Coulomb interaction. Due to the series expansions of the radial functions we get different expressions for the radial density $\rho_{ij}^{DFC}(r)$ depending on the nuclear model used. This leads to an origin behavior of the exchange contributions to the EEIPs, for which different cases have to be considered, which are discussed in the Appendix.

Analogously to the derivation of Eq. (33), for the DFC potentials we get by adding the inhomogeneous contributions (A25) and (A26)—as derived in in Appendix—to the homogeneous part,

[1]The second integral in Eq. (11) was evaluated according to

$$\lim_{\epsilon\to 0}\int_{\epsilon}^{\infty} dr f(r)=\lim_{\epsilon\to 0}\left[\int_0^{\infty} dr f(r)-\int_0^{\epsilon} dr f(r)\right],$$

such that the ϵ-independent expectation value $\langle f(r)\rangle$ enters the expression. The boundary ϵ is chosen such that a Taylor-series expansion for the integrand $f(r)$ converges. This series expansion is constructed from the series expansions of the radial functions.

$$W_i^P(0)=\lim_{r\to 0}[V_i^P(r)+X_i^P(r)/P_i(r)] \tag{35}$$

$$=\langle 1/R\rangle-\langle \rho_{ii}^{DFC}/r\rangle-\begin{cases}\frac{1}{2}\sum_{j,j\neq i}\delta_{(\beta_{ij,min}^P,0)}D_jA_{ij(l_i-l_j)}^{DFC}\left\langle\frac{\rho_{ij}^{DFC}(r)}{r^{\nu_{min}+1}}\right\rangle\frac{a_{k_{j,min},j}^{DFC}}{a_{k_{i,min},i}^{DFC}}, & \text{finite nucleus}\\ \frac{1}{2}\sum_{j,j\neq i}\delta_{(\kappa_i,\kappa_j)}D_jA_{ij0}^{DFC}\left\langle\frac{\rho_{ij}^{DFC}(r)}{r}\right\rangle\frac{a_{0,j}^{DFC}}{a_{0,i}^{DFC}}, & \text{point nucleus},|\kappa_i|=1\\ \infty, & \text{point nucleus, otherwise,}\end{cases} \tag{36}$$

$$W_i^Q(0)=\lim_{r\to 0}[V_i^P(r)+X_i^Q(r)/Q_i(r)] \tag{37}$$

$$=\langle 1/R\rangle-\langle \rho_{ii}^{DFC}/r\rangle-\begin{cases}\frac{1}{2}\sum_{j,j\neq i}\delta_{(\beta_{ij,min}^Q,0)}D_jA_{ij(l_i-l_j)}^{DFC}\left\langle\frac{\rho_{ij}^{DFC}(r)}{r^{\nu_{min}+1}}\right\rangle\frac{b_{m_{j,min},j}}{b_{m_{i,min},i}}, & \text{finite nucleus}\\ \frac{1}{2}\sum_{j,j\neq i}\delta_{(\kappa_i,\kappa_j)}D_jA_{ij0}^{DFC}\left\langle\frac{\rho_{ij}^{DFC}(r)}{r}\right\rangle\frac{b_{0,j}}{b_{0,i}}, & \text{point nucleus},|\kappa_i|=1\\ \infty, & \text{point nucleus, otherwise.}\end{cases} \tag{38}$$

The third index of the symmetry coefficients results from the possible values of j_i, j_j, and κ_i,κ_j, respectively, under the restrictions included in the Kronecker delta (for details see the Appendix). It can be seen from these equations that the main contribution to the EEIPs at the origin is given by the $\langle 1/R\rangle$ expectation value, which by far dominates the above expressions. Additional contributions can be written in terms of $\langle 1/r^n\rangle$ matrix elements. These small corrections, which cause the shell dependence of the EEIPs, result from the local self-interaction term and the nonlocal exchange interaction only, while the part that concerns the Coulomb interaction (self-interaction included) is equal for all shells.

Furthermore, it is interesting to analyze in case of the DFC EEIPs, whether there is a connection between $W_i^P(r)$ and $W_i^Q(r)$, since this assumption is usually made in the relativistic density functional theory [25]. In general, these two components are equal in their long-range behavior (see Sec. IV for details), but they may be different in the short-range limit. Nevertheless, these EEIPs are identical at the origin in some special cases for the point nucleus; considering the cusp-analogous condition for the case of a point nucleus [24],

$$\frac{b_{0,i}}{a_{0,i}^{DFC}}=\frac{(\alpha_i+\kappa_i)c}{Z}, \tag{39}$$

it follows that

$$\frac{a_{0,i}^{DFC}}{a_{0,j}^{DFC}}=\frac{b_{0,i}}{b_{0,j}} \tag{40}$$

if $\kappa_i=\kappa_j$. Therefore, we obtain from Eqs. (36) and (38)

$$W_i^P(0)=W_i^Q(0), \tag{41}$$

provided $|\kappa_i|=1$. This demonstrates that $W_i^P(r)$ and $W_i^Q(r)$ are equal at the origin for $s_{1/2}$ and $p_{1/2}$ shells in a pointlike nuclear potential. For $|\kappa_i|>1$, $W_i^P(r)$, and $W_i^Q(r)$ are singular at the origin. Note that Eq. (39) does not hold for the case of a finite nucleus, in general.

B. Open-shell atoms

The analysis presented so far is derived for closed-shell atoms only. For open-shell systems, the HF and DFC EEIPs are of a different form. Moreover, Eq. (30) cannot be used, since $D_i^{HF,open}\neq 4l_i+2$ and $D_i^{DFC,open}\neq 2j_i+1$. In spite of this, the same expressions for $W_i^{(S,P,Q)}(0)$ can be used as in the case of closed-shell systems. This is now shown for $W_i^S(0)$; for the DFC EEIPs at the origin, an analogous approach can be used.

Considering atoms with one open shell, we have to distinguish between the HF EEIPs for the open and the closed shells. In the former case the potential is [16]

$$W_i^{S,o}(r,LS)=\sum_j D_jU_{jj0}(r)-U_{ii0}(r)-\frac{1}{2}\sum_{j,j\neq i}\sum_\nu D_jA_{ij\nu}^{HF}U_{ji\nu}(r)\frac{P_j(r)}{P_i(r)}-\sum_{\nu>0}\tilde{\alpha}_{i,k}(LS)U_{ii\nu}(r). \tag{42}$$

Only the coefficients $\tilde{\alpha}_{i,k}(LS)$ depend explicitly on the (LS) state of the system. The summation is over all shells of the

atom. For the closed shells the potential is not explicitly dependent on the (LS) state of the atom,

$$W_i^{S,c}(r,LS)=\sum_j D_j U_{jj0}(r)-U_{ii0}(r) -\frac{1}{2}\sum_{j,j\neq i}\sum_{\nu} D_j A_{ij\nu}(r)U_{ji\nu}(r)\frac{P_j(r)}{P_i(r)} -\sum_{\nu>0}(2l_i+1)A_{ii\nu}(r)U_{ii\nu}(r). \tag{43}$$

At the origin, both potentials lead to the same expression, which is identical with Eq. (33). Differences may occur only by the last sum in these equations, but since $\nu=0$ is excluded, there are no additional short-range contributions.

If the method of configuration averages is used for open-shell systems, the EEIPs may be written as

$$W_i^{S,av}(r)=\sum_j D_j U_{jj0}(r)-U_{ii0}(r)-\frac{D_i-1}{4l_i+1} \times\sum_{\nu>0}(2l_i+1)A_{ii\nu}U_{ii\nu}(r) -\frac{1}{2}\sum_{j,j\neq i} D_j\sum_{\nu} A_{ij\nu}U_{ji\nu}(r)\frac{P_j(r)}{P_i(r)}. \tag{44}$$

The same reasoning as in the former case can be used to show that this equation leads also to Eq. (33) at the origin.

IV. ASYMPTOTIC BEHAVIOR OF HF AND DFC POTENTIALS

The long-range behavior of the EEIPs has been the subject of many investigations [6,13,26,27]. Especially the correct asymptotic behavior of the exchange potentials in the context of the density-functional theory and related methods has often been examined in the nonrelativistic framework (see, for instance, [28]). We briefly recall the analysis for nonrelativistic theory within our approach and extend it to the DFC theory. For large values of r, the EEIPs are dominated by the $1/r$ decay of the potential functions $U_{ij\nu}$ with $\nu=0$ since

$$\lim_{r\to\infty} U_{ij\nu}(r)=\langle\rho_{ij}(r)r^{\nu}\rangle\lim_{r\to\infty} r^{-\nu-1}. \tag{45}$$

Thus, the homogeneous contributions to the EEIPs in the long-range limit may be written as

$$\lim_{r\to\infty} V_i(r)=\frac{1}{r}\sum_j D_j\langle\rho_{jj}\rangle-\frac{D_i}{2}A_{ii0}\langle\rho_{ii}\rangle=\frac{1}{r}\left[\sum_j D_j-1\right], \tag{46}$$

which holds for both the HF and the DFC potentials. The inhomogeneous part is determined by

$$\lim_{r\to\infty}\frac{X_i^S(r)}{P_i(r)}=-\frac{1}{2}\sum_{j,j\neq i} D_j A_{ij\nu_{min}}\langle\rho_{ij}\rangle\lim_{r\to\infty}\left\{\frac{P_j(r)}{r^{1+\nu_{min}}P_i(r)}\right\} =0 \tag{47}$$

within the HF theory and by

$$\lim_{r\to\infty}\frac{X_i^P(r)}{P_i(r)}=\frac{1}{2}\sum_{j,j\neq i} D_j A^{DFC}_{ij\nu_{min}}\langle\rho_{ij}\rangle\lim_{r\to\infty}\left\{\frac{P_j(r)}{r^{1+\nu_{min}}P_i(r)}\right\}=0, \tag{48}$$

$$\lim_{r\to\infty}\frac{X_i^Q(r)}{Q_i(r)}=\frac{1}{2}\sum_{j,j\neq i} D_j A^{DFC}_{ij\nu_{min}}\langle\rho_{ij}\rangle\lim_{r\to\infty}\left\{\frac{Q_j(r)}{r^{1+\nu_{min}}Q_i(r)}\right\}=0, \tag{49}$$

within the DFC theory. The vanishing of contributions from the inhomogeneities $X_i^{(S,P,Q)}(r)$ comes from the use of orthonormal radial functions yielding $\langle\rho_{ij}\rangle=0$. Thus, there are only contributions from the homogeneous part, which is equal in both cases, and we finally obtain

$$\lim_{r\to\infty} W_i^{(S,P,Q)}(r)=\frac{\sum_j D_j-1}{r}=\frac{N-1}{r}. \tag{50}$$

As can be seen from the preceding section, this expression holds for closed- and open-shell systems. If we add the electron-nucleus potential, this is just the potential of the ion, which the electron leaves behind, i.e., $-(Z-N+1)/r$.

V. GRAPHICAL REPRESENTATION OF HF AND DFC EEIPS

In this section, we present the numerically calculated *short-range* behavior of EEIPs, obtained using fully numerical atomic-structure programs for the HF [29] and DFC calculations [30]. The implemented numerical discretization schemes and solution methods are described elsewhere [15,24,29,30]. For the relativistic calculations, the value for the speed of light $c=137.035\,989\,5$ was used [31]. All results were obtained with 2000 inner grid points on a rational (HF calculations) and logarithmic grid (DFC calculations), respectively. Figures 1 and 2 reproduce nicely the analytical results. Particularly, Fig. 1 shows the shell dependence of the EEIPs. Additionally, Fig. 2 shows that the DFC EEIPs are not identical for large and small components. But for $r=0$, the relationship $W_i^P(r)=W_i^Q(r)$ is valid for shells with $|\kappa|=1$, i.e., $j=\{1/2,-1/2\}$. The singularities for shells with other values for j affect only the very first grid points, because the absolute values of the exponents $\beta_{ij,min}$ in Eq. (A16) are very small. Nevertheless, calculations with grid points closer to the origin leave no doubt that singularities occur for shells with $|\kappa|>1$, while the EEIPs $W^P_{np_{1/2}}(r)$ show regular behavior and, furthermore, yield the same values as $W^Q_{np_{1/2}}(r)$ at the first grid point as obtained by Eq. (41).

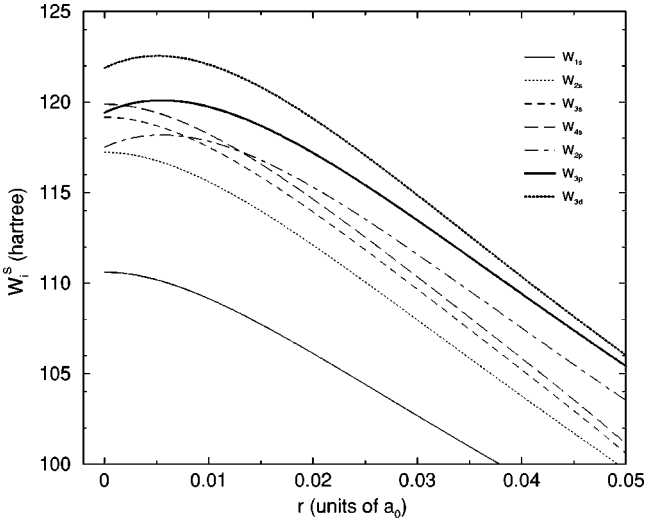

FIG. 1. HF EEIPs for orbitals of Zn ($Z=N=30$). Note that the value for $\langle 1/R \rangle$, which is common in all the shell-dependent potentials, is 142.06.

VI. CONCLUSION

Writing the HF and DFC equations as formally homogeneous differential equations introduces quasilocal EEIPs. An analysis of the short- and long-range behavior shows that the HF and DFC EEIPs can be treated parallel and lead to completely analogous expressions. The main contribution to the value of these potentials at the origin is shell independent and given by the $\langle 1/R \rangle$ expectation value. Shell dependence originates from the contributions of the local self-interaction term and the nonlocal exchange interaction terms and can be ascribed to $\langle 1/r^n \rangle$ matrix elements. The DFC EEIPs additionally depend on the kind of potential used to describe the electron-nucleus interaction, due to its influence on the short-range series expansion of the radial functions, which enter the analysis of the exchange contributions at the origin. We find singularities at the origin for the DFC EEIPs of shells with $|\kappa_i| \neq 1$, if a point-nucleus model is used. However, well-defined expressions can be given for shells with $|\kappa_i| = 1$ (point nucleus) and for all shells, if a finite nucleus model is applied. The relativistic DFC EEIPs for large and small components are not identical, in general, only in the case of a point nucleus, and if $|\kappa_i|=1$ we could prove $W_i^P(0)=W_i^Q(0)$.

Contrary to their behavior at the origin, the EEIPs are shell independent, and within the DFC approach identical for large and small components, in the long-range limit, where they show the Coulomb-type interaction between an electron and the remaining ionized atom with $N-1$ electrons.

Additionally, it is straightforward to apply the analysis presented here to EEIPs resulting from the Breit interaction via potential functions as defined in [32,33], which are used in the Dirac-Fock theory as a relativistic correction to the nonrelativistic instantaneous Coulomb-type electron-electron interaction operator.

The analytical expressions derived here can be used in the construction of local model potentials exhibiting the correct short-range and asymptotic behavior for efficient electronic-structure calculations without evaluating time-consuming two-electron integrals.

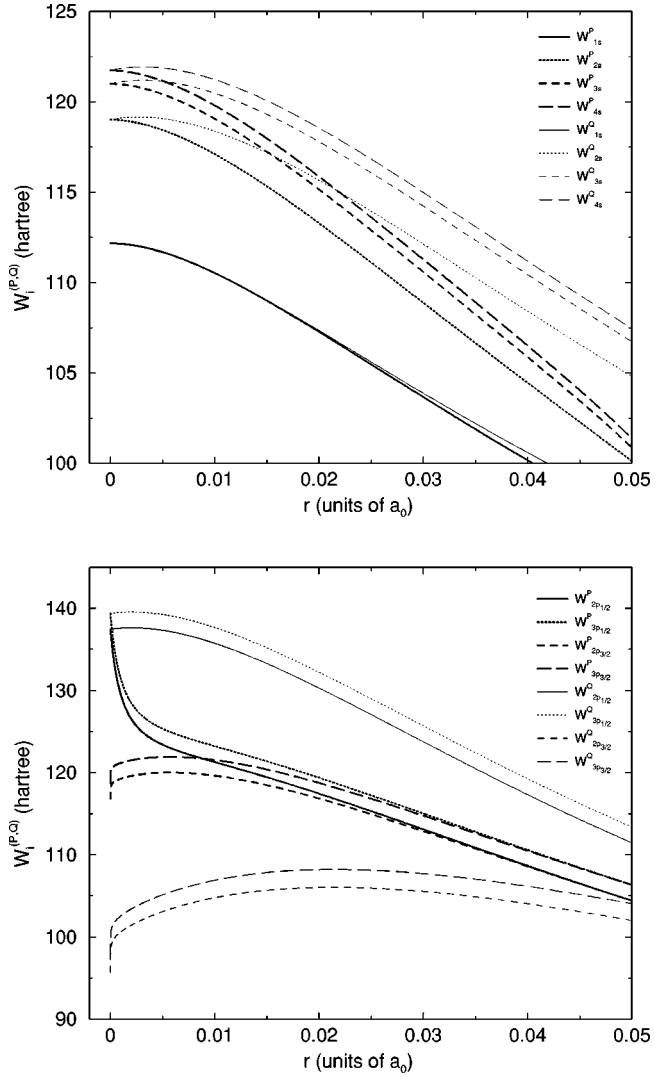

FIG. 2. DFC EEIPs for s and p spinors of Zn ($Z=N=30$) (point nucleus). Note that the value for $\langle 1/R \rangle$, which is common in all the shell-dependent potentials, is 144.47.

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APPENDIX: EXCHANGE INTERACTION AT THE ORIGIN

For the evaluation of the short-range behavior of Eqs. (17), (19), and (20), $\lim_{r\to 0}[V_i(r)+X_i^R(r)/R_i(r)]$ (with R being $\{S,P,Q\}$ and R_i being the corresponding radial function), we used expressions for the origin behavior of $X_i^R(r)/R_i(r)$, which are derived in the following.

1. Nonrelativistic framework

For the determination of $X_i^S(0)/P_i(0)$, we evaluate products of potential functions $U_{ij\nu}(r)$ and ratios of radial functions $P_j(0)/P_i(0)$,

$$\lim_{r_1\to 0}\left[U_{ij\nu}(r_1)\frac{P_j(r_1)}{P_i(r_1)}\right] = \lim_{r_1\to 0}\left[r_1^{m-1}\left(\frac{a_{0,j}^{HF2}}{\nu+l_i+l_j+3}-\frac{a_{0,j}^{HF2}}{l_i+l_j-\nu+2}\right) + r_1^{\nu+l_j-l_i}\left\langle\frac{\rho_{ij}^{HF}(r_2)}{r_2^{\nu+1}}\right\rangle\frac{a_{0,j}^{HF}}{a_{0,i}^{HF}}+O(r_1^m)\right],\quad m=3+2l_j, \tag{A1}$$

where we used the definition of $U_{ij\nu}(r)$ in Eq. (11) and the series expansion, Eq. (25). Only the last term yields nonvanishing contributions for short distances r, provided $\nu=l_i-l_j$ and $l_i\geqslant l_j$ (otherwise this term always vanishes, since negative values for ν are not allowed by the selection rules). The former constraint can easily be understood, since for $\nu>l_i-l_j$ we have $\lim_{r_1\to 0}(r_1^{\nu+l_j-l_i})=0$, and $\nu<l_i-l_j$ is not allowed due to the selection rules. Summarizing the above results, we get

$$\lim_{r\to 0}\left[U_{ij\nu}(r)\frac{P_j(r)}{P_i(r)}\right]=\begin{cases}0, & \nu\neq l_i-l_j\\ \langle\rho_{ij}^{HF}/r^{\nu+1}\rangle\dfrac{a_{0,j}^{HF}}{a_{0,i}^{HF}}, & \nu=l_i-l_j\end{cases} \tag{A2}$$

and we are now able to evaluate $X_i^S(r)/P_i(r)$ in Eq. (32) for $r=0$,

$$\lim_{r\to 0}\left[\frac{X_i^S(r)}{P_i(r)}\right]=-\frac{1}{2}\sum_{j;\{j\neq i,l_j\leqslant l_i\}}D_jA_{ij(l_i-l_j)} \times\langle\rho_{ij}^{HF}/r^{l_i-l_j+1}\rangle\frac{a_{0,j}^{HF}}{a_{0,i}^{HF}}, \tag{A3}$$

to arrive at Eq. (33).

2. Relativistic framework

The exchange-interaction contributions to the EEIPs in the DFC theory at the origin require to consider different cases due to different first exponents in the series expansions for the radial functions resulting from different nucleus models. In case of the pointlike nucleus model, we have [34]

$$\alpha_i=\sqrt{\kappa_i^2-\frac{Z^2}{c^2}}, \tag{A4}$$

while for finite nucleus models α_i is a non-negative integer [24]

$$\alpha_i=|\kappa_i|. \tag{A5}$$

In the latter case, either a_0^{DFC} or b_0 in Eq. (26) may be zero, dependent on $\mathrm{sgn}(\kappa_i)$. Thus, one must distinguish the following two cases.

(1) $\kappa>0$, $\alpha=\kappa$: this yields

$$a_0^{DFC}=0\Rightarrow k_{min}=1 \quad\text{and}\quad b_0\neq 0\Rightarrow m_{min}=0. \tag{A6}$$

(2) $\kappa<0$, $\alpha=-\kappa$: this yields

$$a_0^{DFC}\neq 0\Rightarrow k_{min}=0 \quad\text{and}\quad b_0=0\Rightarrow m_{min}=1. \tag{A7}$$

Here we introduced k_{min} and m_{min}, which denote the lowest indices k and m in Eq. (26) with nonzero values for the coefficients a_k^{DFC} and b_m. Both k_{min} and m_{min} are zero in case of a point nucleus. In analogy to the HF treatment, we therefore obtain

$$\lim_{r_1\to 0}\left[U_{ij\nu}(r_1)\frac{P_j(r_1)}{P_i(r_1)}\right]=\lim_{r_1\to 0}\left[r_1^{\beta_{ij}^P}\left\langle\frac{\rho_{ij}^{DFC}(r_2)}{r_2^{\nu+1}}\right\rangle\frac{a_{k_{j,min},j}^{DFC}}{a_{k_{i,min},i}^{DFC}}\right], \tag{A8}$$

$$\lim_{r_1\to 0}\left[U_{ij\nu}(r_1)\frac{Q_j(r_1)}{Q_i(r_1)}\right]=\lim_{r_1\to 0}\left[r_1^{\beta_{ij}^Q}\left\langle\frac{\rho_{ij}^{DFC}(r_2)}{r_2^{\nu+1}}\right\rangle\frac{b_{m_{j,min},j}}{b_{m_{i,min},i}}\right], \tag{A9}$$

where we already skipped the terms vanishing in the short-range limit. The exponents β are defined by the following expressions:

$$\beta_{ij}^P=\nu+(\alpha_j+k_{j,min})-(\alpha_i+k_{i,min}), \tag{A10}$$

$$\beta_{ij}^Q=\nu+(\alpha_j+m_{j,min})-(\alpha_i+m_{i,min}). \tag{A11}$$

Obviously, in the case of an external potential of a point nucleus both expressions are equal, $\beta_{ij}^P=\beta_{ij}^Q=\beta_{ij}$. The next task is the determination of the lowest possible values $\beta_{ij,min}$, since only $\beta_{ij,min}=0$ results in regular, nonvanishing contributions at the origin.

a. The case of a point nucleus

In the presence of the external potential of a point nucleus, the exponents α_i are noninteger, while the allowed values of ν are always integers. Therefore, additional cases must be considered in order to determine those, which lead to nonvanishing contributions at the origin in Eqs. (A8) and (A9), i.e., which yield exponents $\beta_{ij}\not>0$.

(a) $|\kappa_i|=|\kappa_j|$: The lowest possible value for ν is[2] $\nu_{min}=0$, so that

$$\beta_{ij,min}=0. \tag{A12}$$

(b) $|\kappa_i|<|\kappa_j|$: Here we have $\nu_{min}=j_j-j_i=|\kappa_j|-|\kappa_i|$, and therefore

[2]The quantum numbers j_i and κ_i are related by $j_i=|\kappa_i|-1/2$ and $\nu_{min}=|j_i-j_j|=||\kappa_i|-|\kappa_j||$.

$$\beta_{ij,min}=|\kappa_j|-|\kappa_i|-\left(|\kappa_i|\sqrt{1-\frac{Z^2}{c^2\kappa_i^2}}-|\kappa_j|\sqrt{1-\frac{Z^2}{c^2\kappa_j^2}}\right) \tag{A13}$$

$$\approx 2|\kappa_j|-2|\kappa_i|+\frac{Z^2}{2c^2}\left(\frac{1}{|\kappa_i|}-\frac{1}{|\kappa_j|}\right)>0. \tag{A14}$$

In the last transformation, we utilized the Taylor-series expansion $\sqrt{1+x}=1+x/2+O(x^2)$, which converges for $|x|<1$.

(c) $|\kappa_i|>|\kappa_j|$: This leads to EEIP singularities, since $\nu_{min}=|\kappa_i|-|\kappa_j|$, from which we obtain

$$\beta_{ij,min}=|\kappa_i|-|\kappa_j|-\left(|\kappa_i|\sqrt{1-\frac{Z^2}{c^2\kappa_i^2}}-|\kappa_j|\sqrt{1-\frac{Z^2}{c^2\kappa_j^2}}\right) \tag{A15}$$

$$\approx \frac{Z^2}{2c^2}\left(\frac{1}{|\kappa_i|}-\frac{1}{|\kappa_j|}\right)<0. \tag{A16}$$

This shows that all EEIPs $W_i^P(r), W_i^Q(r)$ [see Eqs. (19) and (20)], in which contributions with $|\kappa_i|>|\kappa_j|$ occur, i.e., all EEIPs except those with the minimal $|\kappa_i|=1$, behave nonregular at the origin.

Only for $|\kappa_i|=1$ we find a regular short-range behavior of the EEIPs for the case of a point nucleus. In this case, we find nonvanishing contributions only for $|\kappa_j|=|\kappa_i|=1$, where $\nu_{min}+j_i+j_j=2j_i$ is odd. Thus, these contributions occur only if $\mathrm{sgn}(\kappa_i)=\mathrm{sgn}(\kappa_j)$ and therefore $\kappa_i=\kappa_j=\pm 1$.

b. The case of a finite nucleus

In the presence of an external potential of a finite nucleus, the values $\beta_{ij,min}$ are different for large and small component in accordance with Eqs. (A10) and (A11). They are dependent on $\mathrm{sgn}(\kappa)$, which can be seen by means of Eqs. (A6) and (A7). Writing Eqs. (A10) and (A11) explicitly for all possible combinations $\{\mathrm{sgn}(\kappa_i),\mathrm{sgn}(\kappa_j)\}$, we obtain

$$\beta_{ij}^P=\begin{cases}\nu+|\kappa_j|-|\kappa_i|, & \mathrm{sgn}(\kappa_i)=\mathrm{sgn}(\kappa_j)\\ \nu+|\kappa_j|-|\kappa_i|-1, & \kappa_i>0\wedge\kappa_j<0\\ \nu+|\kappa_j|-|\kappa_i|+1, & \kappa_i<0\wedge\kappa_j>0,\end{cases} \tag{A17}$$

$$\beta_{ij}^Q=\begin{cases}\nu+|\kappa_j|-|\kappa_i|, & \mathrm{sgn}(\kappa_i)=\mathrm{sgn}(\kappa_j)\\ \nu+|\kappa_j|-|\kappa_i|-1, & \kappa_i<0\wedge\kappa_j>0\\ \nu+|\kappa_j|-|\kappa_i|+1, & \kappa_i>0\wedge\kappa_j<0.\end{cases} \tag{A18}$$

It is useful to regard the lowest possible values ν_{min}, since $\nu\geqslant|j_i-j_j|$ has to be fulfilled as well as the constraint concerning the sum $\nu+j_i+j_j$, so that

$$\nu_{min}=\begin{cases}||\kappa_i|-|\kappa_j||, & \mathrm{sgn}(\kappa_i)=\mathrm{sgn}(\kappa_j)\\ ||\kappa_i|-|\kappa_j||+1, & \mathrm{sgn}(\kappa_i)\neq\mathrm{sgn}(\kappa_j),\end{cases} \tag{A19}$$

since $|j_i-j_j|+j_i+j_j=||\kappa_i|-|\kappa_j||+|\kappa_i|+|\kappa_j|-1$ is always odd. Combining Eqs. (A17), (A18), and (A19) yields

$$\beta_{ij,min}^P=\begin{cases}||\kappa_i|-|\kappa_j||+|\kappa_j|-|\kappa_i|, & \mathrm{sgn}(\kappa_i)=\mathrm{sgn}(\kappa_j)\\ ||\kappa_i|-|\kappa_j||+|\kappa_j|-|\kappa_i|, & \kappa_i>0\wedge\kappa_j<0\\ ||\kappa_i|-|\kappa_j||+|\kappa_j|-|\kappa_i|+2, & \kappa_i<0\wedge\kappa_j>0,\end{cases} \tag{A20}$$

$$\beta_{ij,min}^Q=\begin{cases}||\kappa_i|-|\kappa_j||+|\kappa_j|-|\kappa_i|, & \mathrm{sgn}(\kappa_i)=\mathrm{sgn}(\kappa_j)\\ ||\kappa_i|-|\kappa_j||+|\kappa_j|-|\kappa_i|, & \kappa_i<0\wedge\kappa_j>0\\ ||\kappa_i|-|\kappa_j||+|\kappa_j|-|\kappa_i|+2, & \kappa_i>0\wedge\kappa_j<0.\end{cases} \tag{A21}$$

These expressions may be investigated subject to the absolute values of the κ quantum numbers,

$$||\kappa_i|-|\kappa_j||+|\kappa_j|-|\kappa_i|=\begin{cases}0, & |\kappa_i|\geqslant|\kappa_j|\\ 2|\kappa_j|-2|\kappa_i|>0, & |\kappa_i|<|\kappa_j|.\end{cases} \tag{A22}$$

Thus, the lowest exponents $\beta_{ij,min}$ are for the case of a finite nucleus

$$\beta_{ij,min}^P=\begin{cases}0, & \mathrm{sgn}(\kappa_i)=\mathrm{sgn}(\kappa_j)\wedge|\kappa_i|\geqslant|\kappa_j|\\ 0, & \kappa_i>0\wedge\kappa_j<0\wedge|\kappa_i|\geqslant|\kappa_j|\\ \beta_{ij,min}^P>0, & \text{otherwise},\end{cases} \tag{A23}$$

$$\beta_{ij,min}^Q=\begin{cases}0, & \mathrm{sgn}(\kappa_i)=\mathrm{sgn}(\kappa_j)\wedge|\kappa_i|\geqslant|\kappa_j|\\ 0, & \kappa_i<0\wedge\kappa_j>0\wedge|\kappa_i|\geqslant|\kappa_j|\\ \beta_{ij,min}^Q>0, & \text{otherwise}.\end{cases} \tag{A24}$$

It can easily be seen that in contrast to the point-nucleus case, there exist no singularities in the EEIPs in case of a finite nucleus. Hence, an analytical expression for the EEIPs at the origin can be determined for a finite nucleus, and for a point nucleus, as far as shells with $|\kappa_i|=1$ are concerned.

To evaluate the inhomogeneous terms in Eqs. (35) and (37) we have to carry out the summation in Eqs. (23) and (24), and obtain in the short-range limit

$$\lim_{r\to 0}\left[\frac{X_i^P(r)}{P_i(r)}\right]=\begin{cases} -\frac{1}{2}\sum_{j,j\neq i}\delta_{(\beta^P_{ij,min},0)}D_jA^{DFC}_{ij\nu_{min}}\left\langle\frac{\rho^{DFC}_{ij}}{r^{\nu_{min}+1}}\right\rangle\frac{a^{DFC}_{k_{j,min},j}}{a^{DFC}_{k_{i,min},i}}, & \text{finite nucleus}\\ -\frac{1}{2}\sum_{j,j\neq i}\delta_{(\kappa_i,\kappa_j)}D_jA^{DFC}_{ij0}\left\langle\frac{\rho^{DFC}_{ij}}{r}\right\rangle\frac{a^{DFC}_{0,j}}{a^{DFC}_{0,i}}, & \text{point nucleus, } |\kappa_i|=1\\ -\infty, & \text{point nucleus, otherwise,}\end{cases} \tag{A25}$$

$$\lim_{r\to 0}\left[\frac{X_i^Q(r)}{Q_i(r)}\right]=\begin{cases} -\frac{1}{2}\sum_{j,j\neq i}\delta_{(\beta^Q_{ij,min},0)}D_jA^{DFC}_{ij\nu_{min}}\left\langle\frac{\rho^{DFC}_{ij}}{r^{\nu_{min}+1}}\right\rangle\frac{b_{m_{j,min},j}}{b_{m_{i,min},i}}, & \text{finite nucleus}\\ -\frac{1}{2}\sum_{j,j\neq i}\delta_{(\kappa_i,\kappa_j)}D_jA^{DFC}_{ij0}\left\langle\frac{\rho^{DFC}_{ij}}{r}\right\rangle\frac{b_{0,j}}{b_{0,i}}, & \text{point nucleus, } |\kappa_i|=1\\ -\infty, & \text{point nucleus, otherwise.}\end{cases} \tag{A26}$$

In the analysis that leads to Eq. (A4) it is assumed that there is no EEIP which behaves like $1/r$ or more singular at the origin. Since in the relativistic case the pointlike nucleus model can only be applied for $Z\leqslant c$, the prefactor in Eq. (A16) is always $\leqslant 1$. The term in parentheses in Eq. (A16) is always larger than -1, such that $\beta>-1$. Typical values for the Zn atom are $\beta\approx-0.02$. Therefore, in case of singular behavior of the DFC EEIPs, the series expansions of the radial functions remain unaffected by the weak singularity.

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