Approximating Hamiltonian for Hartree-Fock solutions for nonrelativistic atoms

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In our work we construct a Hamiltonian, whose eigenstates approximate the solutions of the self-consistent Hartree-Fock equations for nonrelativistic atoms and ions. Its eigenvalues are given by completely algebraic expressions and the eigenfunctions are defined by Coulomb wave-function orbitals. Within this approximation we compute the binding energy, ionization potentials, electron density distribution, electron density at the nucleus, and atomic scattering factors of nonrelativistic atoms and ions. The accuracy of our results is comparable with those obtained via the usage of the Hartree-Fock method but does not require solving integrodifferential equations or numerically computing integrals with complex functions. This approach can serve as a good initial approximation for performing more accurate calculations and for the quantitative evaluation of physical parameters that depend on the electron density of atoms. The proposed approach is of interest for various fields of condensed matter physics, plasma physics, and quantum chemistry.

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I. INTRODUCTION

The development of relatively simple and universal, but at the same time sufficiently accurate and effective, methods for describing the electronic structure of atoms and ions is of great interest for numerous applications in condensed matter physics and quantum chemistry [1–6]. One of the most well-known and successful achievements in this field has been the Thomas-Fermi statistical model (TFM) with various corrections [7]. This model forms the basis for applied calculations of the structure of molecules and solids, which are performed using the currently widely used density functional theory (for example, Ref. [8]). The TFM has unique features. It does not contain any empirical parameters. It can be derived by applying the quasiclassical approximation in solving the Hartree-Fock equations for a nonrelativistic multielectron system. Additionally, it is asymptotically accurate as $Z \to \infty$ (Z is the nuclear charge). However, the model also has several well-known disadvantages. These arise from the asymptotic nature of quasiclassics. For instance, it provides an incorrect description of the electron density near the nucleus and in the atom's external region. It also requires significantly more complex equations to account for shell oscillations, and for capturing the individual properties of specific atoms when calculating their observable characteristics [9,10].

The quantitative description of nonrelativistic many-electron atoms relies on the numerical solution of self-consistent equations for single-electron wave functions within the Hartree-Fock model (HFM) [11]. A recent review of studies calculating atomic properties using this method is presented in Ref. [12]. Other numerical approaches for calculating the electronic structure of atoms exist, such as the effective potential method [13] and the algorithm for the direct numerical solution of the Schrödinger equation [14]. Despite the high accuracy of numerical calculations, the construction of approximate analytical expressions for atomic wave functions and other characteristics remains of great interest for many applications.

The most common approach involves Slater-type orbitals [15] and other methods for interpolating numerical results using analytical functions. These functions often have a relatively small number of fitting parameters for each orbital (see Ref. [16]). Analytical models of atoms, where electron wave functions take the form of Coulomb orbitals with phenomenological parameter values such as screening constants or quantum defects, are also used (e.g., Ref. [17]). In Ref. [18], it was shown that these parameters can be calculated for all atoms of the periodic table using the operator method for solving the Schrödinger equation. This calculation enabled the construction of an accurate analytical approximation for atomic scattering factors.

Recently, Refs. [5,6] developed an analytical model of the atom in which atomic characteristics are determined by integrals with Coulomb orbitals. However, it requires calculation of a large number of integrals with special functions, which becomes cumbersome in higher orders of perturbation theory. This limits the ability to analytically study the dependence of atomic properties on the nuclear charge.

In this paper, we propose a new approach to calculate the characteristics of nonrelativistic atoms and ions without solving differential equations or computing integrals with numerical functions. Our method does not rely on interpolating solutions of the Hartree-Fock equations. Instead, it involves constructing a Hamiltonian whose eigenstates approximate

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these solutions. Known as the method of approximating Hamiltonians [19], this approach has proven effective in statistical physics. The eigenfunctions of the Hamiltonian constructed in our work are defined by a set of Coulomb orbitals. The eigenvalues are determined through algebraic expressions. Using this Hamiltonian, we can address various problems, making this approach a viable alternative to the HFM for performing mass calculations. Our method is particularly useful in applications such as computer codes for plasma simulations, such as CRETIN [20], FLYCHK [21], and LASNEX-DCA [22]. In these cases, the TFM is used to determine the electrostatic potential [23]. Our approach is also applicable in crystallography for calculating x-ray scattering factors [24], where fits of electronic density are utilized.

In our previous work [5], an atomic model was also considered that allows approximating HFM results. That work used the same effective charge for all electrons of a given atom. In this work, the dependence of the effective charge on quantum numbers is taken into account, which allowed us to simplify the calculations and improve the accuracy. Hydrogenlike wave functions are well known and are often used in atomic calculations and average atom models. For example, in Ref. [10], the trial potential method is described. However, the effective charge and parameters of the trial potential were calculated by means of an iteration scheme instead of algebraic formulas in our model.

As shown in the paper, the usage of the approximating Hamiltonian allows one to calculate binding energy for atoms or ions with any nuclear charge with relative accuracy $\delta < 1\%$ compared to the HFM results. It also enables finding the wave function and electron density, which have correct asymptotics at small and large distances from the nucleus and describe shell oscillations. Additionally, it allows the calculation of ionization potential and atomic form factors that are in good agreement with HFM results.

The paper is organized as follows: In Sec. II, the derivation of the approximating Hamiltonian is discussed, and its eigenvalues and eigenfunctions are determined. Section III presents the results that can be obtained for the observable characteristics of atoms and ions based on this Hamiltonian.

II. APPROXIMATING HAMILTONIAN FOR NONRELATIVISTIC ATOM

Let us consider the Hamiltonian of a nonrelativistic atom in the second-quantized representation, where we use as a basis Coulomb orbitals $|\lambda\rangle = \psi_\lambda(\boldsymbol{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)\chi_s$ with quantum numbers $\lambda = \{nlms\}$. Assume that these orbitals depend on the effective nuclear charge Z_λ, which in the general case differs for different states and does not coincide with the nuclear charge Z (in our work we utilize atomic units; The description of notations is provided in Ref. [5]):

$$\hat{H} = -\sum_\lambda \frac{Z_\lambda^2}{2n^2}\hat{a}_\lambda^\dagger\hat{a}_\lambda - \sum_{\lambda,\lambda'}\langle\lambda'|\frac{Z-Z_\lambda}{r}|\lambda\rangle\hat{a}_{\lambda'}^\dagger\hat{a}_\lambda + \frac{1}{2}\sum_{\lambda,\lambda',\lambda_1,\lambda_1'}\langle\lambda_1,\lambda_1'|\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}|\lambda,\lambda'\rangle\hat{a}_{\lambda_1'}^\dagger\hat{a}_{\lambda_1}^\dagger\hat{a}_{\lambda'}\hat{a}_\lambda. \quad (1)$$

To extract from (1) the approximating Hamiltonian (AH) we use the operator method (OM) of nonperturbative description of quantum systems [25,26]. According to OM, the initial exact Hamiltonian operator is split in such a way that in the zeroth-order approximation only those terms that commute with the number operator $\hat{n}_\lambda = \hat{a}_\lambda^\dagger\hat{a}_\lambda$ are kept. The remaining parts of the exact Hamiltonian are treated as a perturbation. In our particular problem, the operator in the zeroth-order approximation takes the following form:

$$\begin{aligned}\hat{H}_0 &= -\sum_\lambda \frac{Z_\lambda^2}{2n^2}\hat{n}_\lambda - \sum_\lambda\langle\lambda|\frac{Z-Z_\lambda}{r}|\lambda\rangle\hat{n}_\lambda \\ &\quad + \sum_{\lambda\geqslant\lambda'}\langle\lambda,\lambda'|\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}|\lambda,\lambda'\rangle\hat{n}_\lambda\hat{n}_{\lambda'} \\ &\quad - \sum_\lambda\langle\lambda,\lambda|\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}|\lambda,\lambda\rangle\hat{n}_\lambda \\ &= -\sum_\lambda\left[\frac{Z_\lambda^2}{2n^2} + \frac{(Z-Z_\lambda)}{n^2}Z_\lambda\right]\hat{n}_\lambda \\ &\quad + \frac{1}{2}\sum_{\lambda\neq\lambda'}\langle\lambda,\lambda'|\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}|\lambda,\lambda'\rangle\hat{n}_\lambda\hat{n}_{\lambda'}. \end{aligned} \quad (2)$$

The Hamiltonian (2) includes rather cumbersome matrix elements of the electron interaction operator. However, it can be simplified and reduced to an algebraic form using the ansatz we postulated (For the explanation, see below). This approximation reduces two-particle matrix elements to single-particle ones and significantly simplifies all calculations. To express this relationship, let us isolate the quantum number of a shell, i.e., $|\lambda\rangle = |n,\mu\rangle$, where $\{\mu\} = \{lms\}$. Then, the following approximate equality can be written:

$$\begin{aligned}&\int d\boldsymbol{r}_1\int d\boldsymbol{r}_2\psi_{n,\mu}^2(\boldsymbol{r}_1)\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\psi_{n',\mu'}^2(\boldsymbol{r}_2) \\ &\quad\approx k_{n'l'}\int d\boldsymbol{r}_1\psi_{n,\mu}^2(\boldsymbol{r}_1)\frac{1}{r_1} = Z_\lambda\frac{k_{n'l'}}{n^2}, \\ &k_{nl} = 1-\frac{\alpha}{n}-\beta\frac{l(l+1)}{n^2}, \quad n'<n. \end{aligned} \quad (3)$$

here, α,β are empirical parameters. Their numerical values will be determined below. The obtained relation is based on the fact that the average radius of the shell is determined mainly by the quantum number n, so $\langle n'|r_2|n'\rangle \ll \langle n|r_1|n\rangle$ and it can be neglected with an accuracy of corrections that define the coefficient k.

For electrons within the same layer $n' = n$, we use the following ansatz, which also allows one to express two-particle operators through single-particle operators:

$$\begin{aligned}&\langle n,\mu;n,\mu'|\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}|n,\mu;n,\mu'\rangle \\ &\quad\approx\frac{5}{16}\langle n,\mu;n,\mu'|\frac{k'_{nl}}{r_1}+\frac{k'_{nl'}}{r_2}|n,\mu;n,\mu'\rangle \\ &\quad=\frac{5}{16n^2}(Z_{nl}k'_{nl'}+Z_{nl'}k'_{nl}), \\ &k'_{nl} = 1+\beta\frac{l(l+1)}{n^2}. \end{aligned} \quad (4)$$

As a result, the operator (2) is approximately represented as

$$\hat{H}_0 \approx \hat{H}_A = -\sum_\lambda \left[\frac{Z_\lambda^2}{2n^2} + \frac{(Z-Z_\lambda)}{n^2} Z_\lambda\right]\hat{n}_\lambda + \sum_{\lambda>\lambda',n>n'} \frac{Z_\lambda}{n^2} \times k_{\lambda'}\hat{n}_\lambda\hat{n}_{\lambda'} + \frac{5}{16}\sum_{\lambda>\lambda',n=n'} \frac{Z_\lambda}{n^2} k'_{\lambda'}\hat{n}_\lambda\hat{n}_{\lambda'}. \quad (5)$$

Consequently, the AH takes diagonal form and its eigenfunctions are state vectors with a specific set of occupation numbers g_λ, which are 0 or 1. They are determined by the eigenvalues of the particle number operators:

$$\begin{aligned} \hat{H}_A|\{g_\lambda\}\rangle &= E(Z,N,Z_\lambda)|\{g_\lambda\}\rangle, \\ \hat{n}_\lambda|\{g_\lambda\}\rangle &= g_\lambda|\{g_\lambda\}\rangle, \\ \sum_\lambda g_\lambda &= N. \end{aligned} \quad (6)$$

The effective charge will be determined in accordance with the OM [26]. Namely, Z_λ is determined from the fact that the eigenvalues should not depend on its particular value for any given quantum number λ. This implies that

$$\frac{\partial E(Z,N,Z_\lambda)}{\partial Z_\lambda} = 0, \quad (7)$$

for any λ.

Therefore, in order to determine the Z_λ we use Eq. (5) and calculate the derivative with respect to Z_λ. From this equation we determine the value of Z_λ, which reads

$$Z_\lambda = Z - \sum_{\lambda'} g_{\lambda'}\, k_{n,l'} - \frac{5}{16}\left(\sum_{\lambda''} g_{\lambda''}\, k'_{n,l''} - k'_{nl}\right). \quad (8)$$

Here, we use the following notations for the sums:

$$\begin{aligned} \sum_{\lambda'} &= \sum_{n'=1}^{n-1}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}\sum_{s'=\pm1}, \\ \sum_{\lambda''} &= \sum_{l''=0}^{n-1}\sum_{m''=-l''}^{l''}\sum_{s''=\pm1}. \end{aligned} \quad (9)$$

As the AH is diagonal over the particle number operator, the energy of the system is represented as a sum of Hydrogen-like energies with the charge Z_λ:

$$\begin{aligned} \hat{H}_A &= -\sum_\lambda \frac{Z_\lambda^2}{2n^2}\hat{n}_\lambda, \\ E(Z,N) &= -\sum_\lambda \frac{Z_\lambda^2}{2n^2} g_\lambda. \end{aligned}$$

The Parameters are

$$\alpha = 0.321, \quad \beta = 0.412. \quad (10)$$

The above fully algebraic expression with nonlinear dependence on the occupation numbers corresponds to a model of an atom in which an electron on a layer with quantum numbers λ moves in the field of an effective Coulomb potential with a charge Z_λ. It is equal to the nuclear charge minus the partial screening of electrons of underlying layers [the second term in (8)] and other electrons in the same layer [the third term in (8)]. This expression is consistent with the Hohenberg-Kohn theorem [27], since the energy of the system depends only on single-particle characteristics of electrons in an atom.

Let us now investigate the conditions that allow one to determine the coefficient 5/16 and the constants α and β in (10). The first condition arises from the asymptotic behavior of the atomic energy $E(Z,N)$ in the limit $Z \to \infty$. In this limit of large Z, all shells can be considered fully occupied, meaning that the occupation numbers $g_\lambda = 1$, $n \leqslant n_{\max}$ and $g_\lambda = 0$, $n \geqslant n_{\max}$. In this approximation we can replace the sums with integrals in the expression for Z_λ (8) and perform the integration. We restrict ourselves to the terms with the highest power of n:

$$\begin{aligned} Z_\lambda &\to Z_n \\ &\approx Z - \int_{n_1=1}^{n-1}\int_{l_1=0}^{n_1-1} 2(2l_1+1)\, k_{n,l_1} dn_1 dl_1 \\ &\quad - \frac{5}{16}\int_0^{n-1} (4l+1)\, k'_{n,l} dl = Z - \left(\frac{2}{3}+\frac{\beta}{5}\right)n^3. \end{aligned} \quad (11)$$

Similarly, in the expression for energy (8),

$$\begin{aligned} E(Z) &\approx -\int_{n=1}^{n_{\max}}\int_{l=0}^{n-1} (4l+1)\frac{Z_n^2}{2n^2} dn dl \\ &\approx -\int_{n=1}^{n_{\max}} Z_n^2 dn \approx \left(\frac{4}{63} - \frac{4\beta}{105} + \frac{\beta^2}{175}\right)n_{\max}^7 \\ &\quad + \left(-\frac{1}{3} + \frac{\beta}{10}\right) Z n_{\max}^4 + Z^2 n_{\max}. \end{aligned} \quad (12)$$

The value of $n_{\max}$ is determined from the normalization condition in the same approximation:

$$Z \approx \int_{n=1}^{n_{\max}} 2n^2 dn \approx \frac{2}{3}n_{\max}^3, \quad n_{\max} \approx \left(\frac{3Z}{2}\right)^{1/3}. \quad (13)$$

Then the final result is

$$E \approx -\frac{9}{28}12^{2/3}\left(1 + \frac{\beta}{10} + \frac{\beta^2}{50}\right)Z^{7/3}. \quad (14)$$

If we now compare this expression with the well-known exact asymptotics of the binding energy of a nonrelativistic atom derived from the Thomas-Fermi equation [28],

$$E \approx -0.768\,745 Z^{7/3},$$

we find the value $\beta = 0.412$, which is used in formula (10).

The physical meaning of the coefficient 5/16 and the parameter α describe the screening of the nuclear charge by the electrons. Their values in formula (10) are chosen from the conditions that the largest matrix elements for transitions (10; 10) and (10; 20) calculated by (3) and (4) coincide with their values calculated by using Coulomb orbitals.

Thus, the accuracy of the approximation of the original Hamiltonian by the operator (8) depends on the error in replacing matrix elements (3) and (4). Table I presents the results of calculation of the matrix elements using the exact formulas [5] and the approximate ones (3) and (4) in the range of quantum numbers, where the values of matrix elements can be large.

It shows the difference between the two-particle matrix elements of the interaction operator between electrons calculated

TABLE I. Table of difference between exact [5] and approximate [(3) and (4)] matrix elements.

n′l′ \ nl	10	20	21	30	31	32
10	0	0	0.0845	0.0003	0.0198	0.0424
20	0	0.0059	0.0103	0.0151	0.0010	0.0349
21	0.0845	0.0103	0.0072	0.0125	0.0090	0.0419
30	0.0003	0.0151	0.0125	0.0030	0.0038	0.0059
31	0.0198	0.0010	0.0090	0.0038	0.0018	0.0011
32	0.0424	0.0349	0.0419	0.0059	0.0011	0.0036

in the Coulomb orbitals basis [5],

$$M_{nl}^{n'l'} = \frac{1}{Z}\int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 |\psi_{nl}(\boldsymbol{r}_1)|^2 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} |\psi_{n'l'}(\boldsymbol{r}_2)|^2, \quad (15)$$

and their approximate expressions (3) and (4) through single-particle operators.

As shown by the results in this table, the average error δ for such a substitution is $\delta < 0.01$ a.e.u. (atomic energy units). Then, for an atom with Z electrons, the contribution of the electron-electron interaction to the total energy is determined with an accuracy $\Delta E < \frac{1}{2}Z^2\delta$ a.e.u. Considering that the total energy of such an atom is approximately equal to $E \approx Z^{7/3}$ a.e.u., we find that the relative accuracy of formula (15) in calculation of the atomic energy is $\Delta E/E < Z^{-1/3}\%$. This estimate is confirmed by the numerical evaluation, which is presented in the next section.

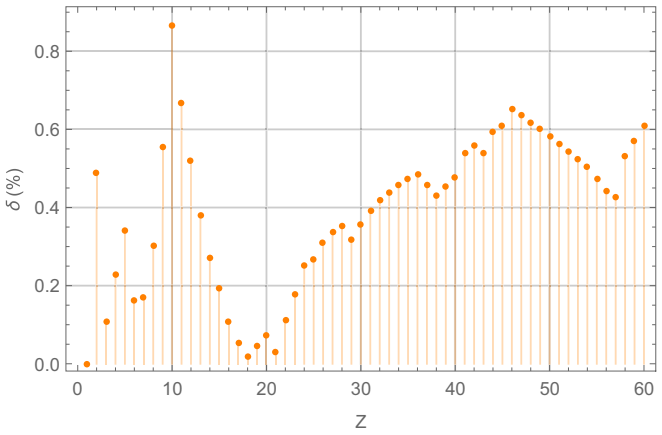

FIG. 1. Relative error (in percentages) between our results (8) and those of the HFM.

III. CALCULATION OF THE ATOMIC CHARACTERISTICS

A. Binding energy

Let us compare our results (8) with the ones via HFM. As shown in Table II and Fig. 1, the algebraic formula (8)

TABLE II. Calculated binding energy and the first three ionization potentials, compared with values obtained from the HFM.

Z	$E_{\rm AH}$	$E_{\rm HF}$	Z_λ	$IP_{\rm AH}$	$IP_{\rm HF}$	Config.	Z	$E_{\rm AH}$	$E_{\rm HF}$	Z_λ	$IP_{\rm AH}$	$IP_{\rm HF}$	Config.
1	0.5	0.5	1	0.5	0.5	$1s$	2	2.84766	2.86168	1.68750	0.84766	0.86029	$1s$
3	7.44078	7.43273	2.68750	2.35732	2.19853	$1s$	3	7.44078	7.43273	1.32099	0.21813	0.20221	$2s$
4	14.6062	14.5730	3.68750	4.57839	4.34926	$1s$	4	14.6062	14.5730	2.00849	0.33513	0.30147	$2s$
			4.68750	7.53795	7.18750	$1s$				5.68750	11.2360	10.6949	$1s$
5	24.6124	24.5291	2.63154	0.42500	0.46324	$2s$	6	37.7498	37.6886	3.25459	0.51456	0.64338	$2s$
			2.69599	0.37704	0.24632	$2p$				3.31904	0.39754	0.33088	$2p$
			6.68750	15.6725	14.8750	$1s$				7.68750	20.8474	19.7353	$1s$
7	54.3092	54.4009	3.87764	0.60382	0.84927	$2s$	8	74.5820	74.8094	4.50069	0.69277	1.07353	$2s$
			3.94209	0.39765	0.42279	$2p$				4.56514	0.37738	0.52206	$2p$
			8.68750	26.7609	25.2794	$1s$				9.68750	33.4128	31.5074	$1s$
9	98.8592	99.4093	5.12374	0.78142	1.31618	$2s$	10	127.432	128.547	5.74680	0.86977	1.58456	$2s$
			5.18819	0.33672	0.62500	$2p$				5.81124	0.27569	0.73529	$2p$
			6.74680	1.58033	2.36397	$2s$				7.74680	2.40447	3.27574	$2s$
11	160.779	161.859	6.81124	0.92489	1.33456	$2p$	12	198.578	199.615	7.81124	1.70167	2.07353	$2p$
			2.61992	0.38133	0.18750	$3s$				3.30742	0.48746	0.25368	$3s$
			8.81124	2.61112	2.97426	$2p$				9.81124	3.65324	3.97794	$2p$
13	240.962	241.877	3.96628	0.58668	0.37132	$3s$	14	288.076	288.854	4.62513	0.68839	0.5	$3s$
			3.99492	0.57302	0.18015	$3p$				4.65378	0.65678	0.23897	$3p$
			10.8112	4.82803	5.09191	$2p$				11.8112	6.13550	6.31618	$2p$
15	340.065	340.719	5.28399	0.79257	0.62868	$3s$	16	397.072	397.505	5.94285	0.89923	0.76471	$3s$
			5.31263	0.73882	0.30515	$3p$				5.97149	0.81914	0.37868	$3p$
			12.8112	7.57564	7.65441	$2p$				13.8112	9.14846	9.10662	$2p$
17	459.243	459.482	6.60170	1.00837	0.90809	$3s$	18	526.722	526.818	7.26056	1.11999	1.05515	$3s$
			6.63035	0.89775	0.45221	$3p$				7.28920	0.97464	0.53309	$3p$
			14.8112	11.1645	11.0074	$2p$				9.26056	1.98547	1.93750	$3s$
19	598.898	599.165	8.26056	1.53670	1.47794	$3s$	20	676.256	676.758	9.28920	1.83187	1.24265	$3p$
			8.28920	1.38501	0.86765	$3p$				3.75065	0.36330	0.19853	$4s$
			9.89077	1.90422	1.44118	$3p$				10.4923	1.97117	1.63971	$3p$

TABLE II. (*Continued*.)

Z	E_{AH}	E_{HF}	Z_λ	IP_{AH}	IP_{HF}	Config.	Z	E_{AH}	E_{HF}	Z_λ	IP_{AH}	IP_{HF}	Config.
21	759.957	759.736	3.98558	0.41551	0.21691	4*s*	22	849.356	848.406	4.22050	0.47116	0.22794	4*s*
			9.94806	1.50930	0.26471	3*d*				10.5496	1.48297	0.31250	3*d*
			11.0939	2.03273	1.83456	3*p*				11.2970	1.61184	1.84559	3*p*
23	944.575	942.884	4.45542	0.53027	0.24265	4*s*	24	1045.97	1043.36	4.23777	0.56121	0.21691	4*s*
			11.1512	1.44359	0.36029	3*d*				11.3543	0.82643	0.23897	3*d*
			12.2970	2.13965	2.23897	3*p*				12.8986	2.18502	2.44853	3*p*
25	1152.95	1149.87	4.92527	0.65882	0.26102	4*s*	26	1266.35	1262.44	5.16020	0.72828	0.27206	4*s*
			12.3543	1.32566	0.44118	3*d*				12.9559	1.24711	0.48162	3*d*
			13.5002	2.22500	2.66176	3*p*				14.1017	2.25957	2.87868	3*p*
27	1386.06	1381.41	5.39512	0.80118	0.28309	4*s*	28	1512.18	1506.87	5.63004	0.87753	0.29044	4*s*
			13.5575	1.15551	0.52206	3*d*				14.1590	1.05086	0.55882	3*d*
			14.3049	1.70380	2.85662	3*p*				15.3049	2.31255	3.33088	3*p*
29	1644.14	1638.96	5.41239	0.91543	0.25368	4*s*	30	1784.18	1777.85	6.09989	1.04058	0.30882	4*s*
			14.3622	0.24648	0.37132	3*d*				15.3622	0.80240	0.62868	3*d*
			16.3049	2.95955	3.94853	3*p*				7.44267	1.28516	0.52941	4*s*
31	1930.79	1923.26	6.77128	1.16190	0.41912	4*s*	32	2084.06	2075.36	17.3622	2.05493	1.44485	3*d*
			16.3622	1.40521	1.02206	3*d*				7.45878	1.26951	0.23529	4*p*
			8.11406	1.41037	0.63971	4*s*				8.78544	1.53753	0.74632	4*s*
33	2244.06	2234.24	18.3622	2.75155	1.91176	3*d*	34	2410.89	2399.87	19.3622	3.49508	2.41912	3*d*
			8.13017	1.38486	0.29044	4*p*				8.80156	1.50080	0.34927	4*p*
			9.45683	1.66663	0.86029	4*s*				10.1282	1.79768	0.97427	4*s*
35	2584.63	2572.44	20.3622	4.28551	2.96324	3*d*	36	2765.36	2752.05	21.3622	5.12284	3.55147	3*d*
			9.47294	1.61734	0.41177	4*p*				10.1443	1.73447	0.47794	4*p*
			11.1282	2.12448	1.30515	4*s*				12.1282	2.46231	1.65441	4*s*
37	2951.79	2938.36	22.3622	6.23899	4.43750	3*d*	38	3145.01	3131.55	12.1443	2.40418	1.01838	4*p*
			11.1443	2.06290	0.73897	4*p*				5.58250	0.55155	0.18382	5*s*
			12.7835	2.53182	1.19853	4*p*				13.4227	2.65874	1.36397	4*p*
39	3346.83	3331.68	5.74569	0.58649	0.20221	5*s*	40	3555.90	3539	5.90889	0.62248	0.21691	5*s*
			12.8157	2.38173	0.20588	4*d*				13.4549	2.47270	0.25735	4*d*
			13.7010	2.51507	1.41544	4*p*				14.3401	2.62631	1.56250	4*p*
41	3773.90	3753.6	5.54777	0.61555	0.20220	5*s*	42	3997.75	3975.55	5.71096	0.65230	0.20956	5*s*
			13.7332	2.24900	0.22426	4*d*				14.3724	2.31815	0.26471	4*d*
			15.3401	3.03517	1.84926	4*p*				15.6185	2.84662	1.86029	4*p*
43	4227.44	4204.79	6.39846	0.73687	0.25	5*s*	44	4467.97	4441.54	6.03734	0.72899	0.22059	5*s*
			15.3724	2.72586	0.41177	4*d*				15.6507	2.44657	0.34191	4*d*
			16.2576	2.95569	2.01103	4*p*				16.5199	2.97998	3.09559	4*s*
45	4714.49	4685.88	6.20053	0.76893	0.22794	5*s*	46	4970.08	4937.92	16.5360	2.70808	2.00735	4*p*
			16.2899	2.50584	0.38235	4*d*				16.5682	2.16359	0.29412	4*d*
			17.5360	3.17167	2.31250	4*p*				18.5360	3.64811	2.65809	4*p*
47	5230.75	5197.7	17.5682	2.61449	0.46324	4*d*	48	5498.92	5465.13	7.21441	0.94882	0.28309	5*s*
			6.52691	0.85201	0.23529	5*s*				18.5682	3.08186	0.67279	4*d*
			19.5360	4.13815	3.09191	4*p*				8.56879	1.14104	0.45955	5*s*
49	5774.64	5740.17	7.89160	1.04422	0.37132	5*s*	50	6057.98	6022.93	20.5682	4.06810	1.26471	4*d*
			19.5682	3.56640	0.96323	4*d*				8.57910	1.13370	0.21691	5*p*
			9.24598	1.23926	0.54412	5*s*				9.92316	1.33890	0.62868	5*s*
51	6348.97	6313.49	21.5682	4.58697	1.57721	4*d*	52	6647.68	6611.8	22.5682	5.12301	1.91176	4*d*
			9.25629	1.22742	0.26838	5*p*				9.93348	1.32200	0.31618	5*p*
			10.6004	1.43996	0.71323	5*s*				11.2775	1.54243	0.80147	5*s*
53	6954.17	6917.98	23.5682	5.67621	2.26103	4*d*	54	7268.49	7232.1	24.5682	6.24657	2.62868	4*d*
			10.6107	1.41743	0.36765	5*p*				11.2879	1.51371	0.41912	5*p*
			12.2775	1.76073	1.05882	5*s*				13.2775	1.98289	1.31985	5*s*
55	7589.54	7553.9	25.5682	7.00972	3.22059	4*d*	56	7918.28	7883.5	13.2879	1.95869	0.84191	5*p*
			12.2879	1.73384	0.62868	5*p*				6.50126	0.52924	0.16544	6*s*
			13.9444	2.06826	0.97059	5*p*				13.8019	2.20091	1.41176	5*s*
57	8256.15	8221.1	6.62350	0.55046	0.18015	6*s*	58	8612.34	8566.9	13.8122	2.17590	0.89338	5*p*
			13.9650	2.00499	0.22794	5*d*				6.88324	0.59693	0.16911	6*s*
			14.0641	2.31405	1.45588	5*s*				14.3263	2.42993	1.49632	5*s*
59	8972.11	8921.2	14.0744	2.28863	0.91912	5*p*	60	9340.45	9283.9	14.3366	2.40411	0.94118	5*p*
			7.07422	0.63230	0.16912	6*s*				7.26521	0.66868	0.17279	6*s*

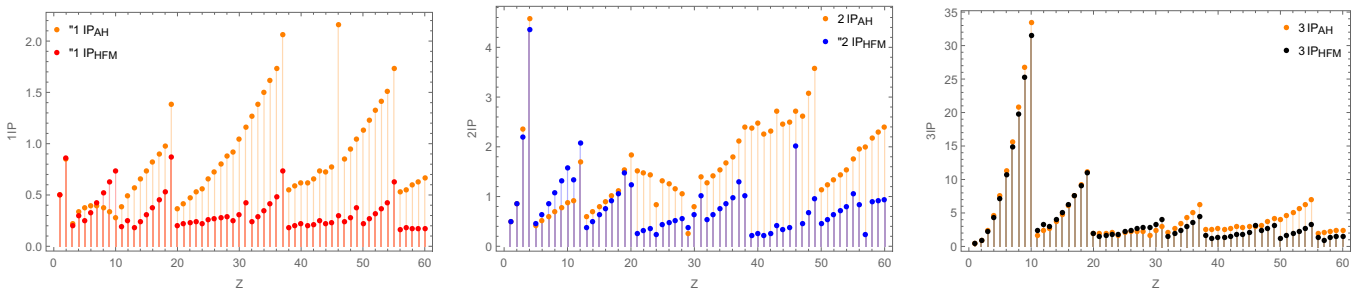

FIG. 2. Comparison of the first three ionization potentials obtained from our results and the HFM.

approximates the results obtained by the HFM for the binding energy of atoms with an accuracy of $\delta < 1\%$ for all Z. The results are presented for $Z \leqslant 60$, when the relativistic corrections are still sufficiently small. It is important to emphasize that the experimental configurations correspond to the minimal atomic energy calculated by the formula (8). Additionally, it is worth noting that our model correctly predicts the filling of electronic shells and corresponds to the Madelung-Klechkowski rule [29,30].

B. Ionization potential

In order to determine the applicability of our results for ions, we calculate the values of partial ionization potentials (IP_{nl}) when an electron is removed from the (n, l) shell [31]. According to Eq. (6), we find

$$\mathrm{IP}_{n,l} = E(Z, N - 1_{n,l}) - E(Z, N). \tag{16}$$

In Table II and Fig. 2, the results for the calculation of the first three ionization potentials (IPs) are presented (in the atomic units). The value of the first IP is comparable in accuracy to that of the binding energy calculations. This means that the computed values are only in qualitative agreement with the HFM results. However, the second and third IPs are calculated with the relative accuracy δ.

C. Electron density distribution

According to the definition of the density operator in the second quantization representation

$$\begin{aligned}\hat{\rho}(\boldsymbol{r}) &= \hat{\Psi}^{\dagger}(\boldsymbol{r})\hat{\Psi}(\boldsymbol{r}),\\ \hat{\Psi}(\boldsymbol{r}) &= \sum_{\lambda}[\hat{a}_{\lambda}\psi_{\lambda}(\boldsymbol{r}, Z) + \hat{a}^{\dagger}_{\lambda}\psi^{*}_{\lambda}(\boldsymbol{r}, Z)],\end{aligned} \tag{17}$$

we find its observable value in the state $|\{g_{\lambda}\}\rangle$,

$$\rho(\boldsymbol{r}) = \sum_{\lambda} g_{\lambda}|\psi_{\lambda}(\boldsymbol{r}, Z_{nl})|^2. \tag{18}$$

Here, Z_{nl} is the effective charge of the shell calculated by formula (8), and the normalized Coulomb orbitals are defined by the well-known formulas

$$\begin{aligned}\psi_{\lambda}(\boldsymbol{r}, Z) &= N_{nl}R_{nl}(r, Z)Y_{lm}(\theta, \phi)\chi_s,\\ R_{nl}(r) &= \left(\frac{2Zr}{n}\right)^{l} e^{-\frac{Zr}{n}} F\left(-n + l + 1, 2l + 2, \frac{2Zr}{n}\right),\\ N_{nl} &= \frac{1}{(2l+1)!}\sqrt{\frac{(n+l)!}{2n(n-l-1)!}}\left(\frac{2Z}{n}\right)^{3/2}.\end{aligned} \tag{19}$$

here, $F(a, c, x)$ is the confluent hypergeometric function. $Y_{lm}(\theta, \phi)$ is the spherical harmonic, and χ_s is the spinor.

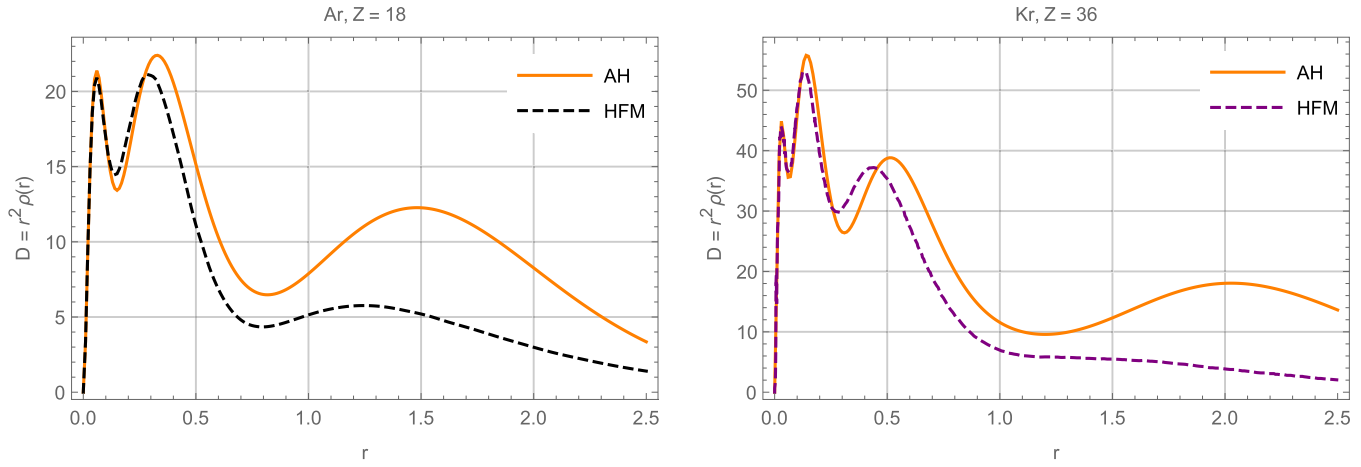

FIG. 3. The radial electron densities for argon (the left panel) and krypton (the right panel), compared with those obtained from the HFM.

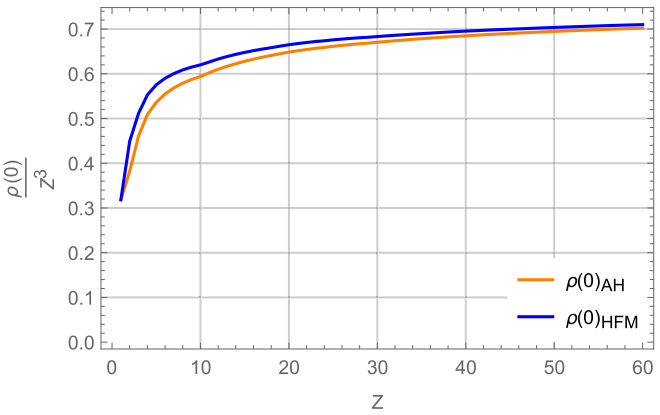

FIG. 4. Comparison of the electron density at the atomic nucleus as computed by our method and by the HFM.

In particular, for atoms with a closed shell, the electron density is spherically symmetric and is given by

$$\rho(r) = \sum_{nl} \frac{2l+1}{2\pi} |N_{nl} R_{nl}(r, Z_{nl})|^2. \tag{20}$$

Figure 3 shows a comparison of the radial electron density $D(r) = r^2\rho(r)$ calculated based on the function (20) and within the framework of the HFM.

Another important observable characteristic for various applications (such as isomer shift [32], and nuclear magnetic resonance [33]) is the electron density at the atomic nucleus (as $r \to 0$). In our approximation, only orbitals with $l = 0$ contribute to this quantity. Thus we find the expression

$$\rho(0) = \sum_{n00s} \frac{g_{n00s}}{4\pi} |N_{n0} R_{n0}(0, Z_{n0})|^2 = \sum_{n00s} \frac{g_{n00s}}{\pi} \left(\frac{Z_{n0}}{n}\right)^3. \tag{21}$$

Figure 4 compares the results obtained on the basis of (21) and within the framework of the HFM.

D. Atomic scattering factors

The atomic scattering factors, which are of significant importance for X-ray crystallography [34], are determined by the Fourier transform of the electron density. In our model, they can be calculated analytically using the formulas given in Ref. [5],

$$f(q) = \sum g_{nl} F_{nl}(Z_{nl}, q), \quad \xi_{nl} = \frac{2Z_{nl}}{n}, \tag{22}$$

$$F_{nl} = -C_{nl} \xi^{2l+3} \frac{(n-l-1)!(n+l)!}{2n} \times \sum_{k,m=0}^{n-l-1} \frac{\xi^{k+m}}{(2l+k+1)!(2l+m+1)!k!m!} \times \frac{d^{2l+1+k+m}}{d\xi^{2l+1+k+m}} \frac{1}{\xi^2 + q^2}, \tag{23}$$

where $f(q)$ is the atomic scattering factor, q is the transverse wave vector associated with the scattering angle θ,

$$q = 4\pi s a_B, \quad s = \sin\theta/\lambda \ (\text{Å}^{-1}),$$

$a_B = 0.529\,177$ Å^{-1} the Bohr radius, and C_{nl} is the normalization coefficient at $q = 0$,

$$C_{nl} = \left[\sum_{k,m=0}^{n-l-1} \frac{\xi^{k+m}}{(2l+k+1)!(2l+m+1)!k!m!} \xi^{2l+3} \times \frac{(n-l-1)!(n+l)!}{2n} \frac{d^{2l+1+k+m}}{d\xi^{2l+1+k+m}} \frac{1}{\xi^2} \right]^{-1}. \tag{24}$$

In Fig. 5, the results calculated using formula (22) are compared with numerical data obtained from solutions of the HFM [35].

IV. CONCLUSION

In our work we developed a new approach on how to approximate the solutions of the self-consistent Hartree-Fock equations for nonrelativistic atoms and ions. It is based on the approximating Hamiltonian $\hat{H}_0$, whose eigenfunctions are given by the Coulomb orbitals and are a good approximation

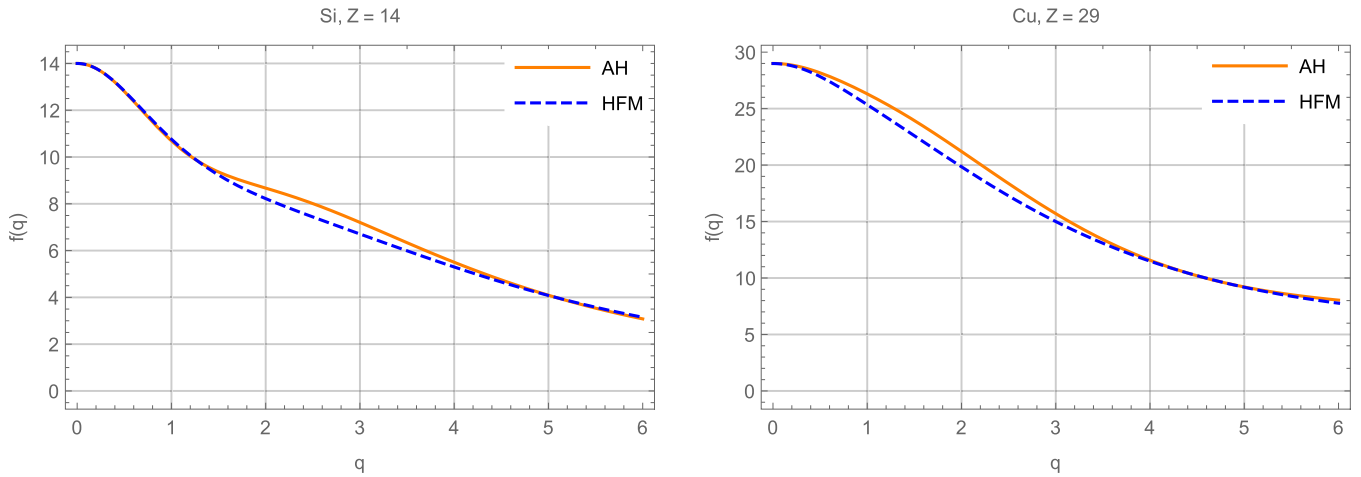

FIG. 5. The atomic scattering factors for neutral Si (the left panel) and Cu (the right panel). Orange solid and blue dashed lines indicate our results and HFM values, respectively.

to HFM solutions. The Hamiltonian is represented by a sum of single-particle operators, and its eigenvalues are determined by a fully algebraic expression. They offer a good approximation for the atomic binding energy. It is shown that within our approach one can analytically calculate various observable characteristics of atoms and ions. In particular, the ionization potential, electron density distribution, and atomic scattering factor are in good agreement with the results obtained in the HFM approximation.

Furthermore, it is important to emphasize that the representation of the single-electron approximation in the form of an eigenvalue problem instead of a system of nonlinear integrodifferential equations allows one to use the standard form of quantum mechanical perturbation theory over the operator $\hat{V} = \hat{H} - \hat{H}_0$. This perturbation operator takes into account correlation effects in multi-electron systems. We also suppose that our approach can be generalized for molecules. Additional derivations, numerical details, and supplementary figures are presented in the Supplemental Material [36].

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DATA AVAILABILITY

The data that support the findings of this article are openly available [37].

[1] G. A. Petersson, A. Bennet, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, and J. Mantzaris, A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements, J. Chem. Phys. **89**, 2193 (1988); G. A. Petersson and M. A. Al-Laham, A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms, *ibid.* **94**, 6081 (1991).

[2] F. Jensen, *Introduction to Computational Chemistry* (Wiley, Hoboken, NJ, 2007).

[3] A. Szabo and N. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, *Dover Books on Chemistry* (Dover, New York, 1989).

[4] C. C. J. Roothaan, New developments in molecular orbital theory, Rev. Mod. Phys. **23**, 69 (1951).

[5] O. D. Skoromnik, I. D. Feranchuk, A. U. Leonau, and C. H. Keitel, Analytic model of a multi-electron atom, J. Phys. B: At. Mol. Opt. Phys. **50**, 245007 (2017).

[6] K. D. Dzikowski, O. D. Skoromnik, I. D. Feranchuk, N. S. Oreshkina, and C. H. Keitel, Relativistic effective charge model of a multi-electron atom, J. Phys. B: At. Mol. Opt. Phys. **54**, 115002 (2021).

[7] L. H. Thomas, The calculation of atomic fields, Math. Proc. Cambridge Philos. Soc. **23**, 542 (1927); E. R. Fermi, Un metodo statistico per la determinazione di alcune prioprietá dell atomo, Rend. Accad. Naz. Lincei **6**, 602 (1927) .

[8] E. Engel, *Density Functional Theory* (Springer, Berlin, 2011).

[9] D. A. Kirzhnits, Y. E. Lozovik, and G. V. Shpatakovskaya, Statistical model of matter, Sov. Phys. Usp. **18**, 649 (1975).

[10] V. U. Arnold, F. Nikiforov, and V. G. Novikov, *Quantum-Statistical Models of Hot Dense Matter: Methods for Computation Opacity and Equation of State* (Springer, Berlin, 2005).

[11] D. R. Hartree, The wave mechanics of an atom with a non-Coulomb central field. Part I. Theory and methods, Math. Proc. Cambridge Philos. Soc. **24**, 89 (1928); The wave mechanics of an atom with a non-Coulomb central field. Part II. Some results and discussion, **24**, 111 (1928); V. Fock, Näherungsmethode zur lösung des quantenmechanischen mehrkörperproblems, Z. Phys. **61**, 126 (1930).

[12] C. Froese-Fischer, T. Brage, and P. Jonsson, *Computational atomic Structure: An MCHF Approach* (Routledge, New York, 2022).

[13] T. Grabo, T. Kreibich, and E. Gross, Optimized effective potential for atoms and molecules, Mol. Eng. **7**, 27 (1997).

[14] L. Zhang and T. E. Simos, An efficient numerical method for the solution of the Schrödinger equation, Adv. Math. Phys. **2016**, 8181927 (2016).

[15] J. C. Slater, Analytic atomic wave functions, Phys. Rev. **42**, 33 (1932).

[16] J. Zhang and N. J. Mauser, Optimal slater-determinant approximation of fermionic wave functions, Phys. Rev. A **94**, 032513 (2016).

[17] A. E. S. Green, D. L. Sellin, and A. S. Zachor, Analytic independent-particle model for atoms, Phys. Rev. **184**, 1 (1969).

[18] I. D. Feranchuk, L. I. Gurskii, L. I. Komarov, O. M. Lugovskaya, F. Burgäzy, and A. Ulyanenkov, A new method for calculation of crystal susceptibilities for X-ray diffraction at arbitrary wavelength, Acta Cryst. A **58**, 370 (2002).

[19] N. N. Bogolyubov, J. Brankov, V. A. Zagrebnov, A. M. Kurbatov, and N. Tonchev, Some classes of exactly soluble models of problems in quantum statistical mechanics: The method of the approximating Hamiltonian, Russ. Math. Surv. **39**, 1 (1984).

[20] H. A. Scott, Cretin—a radiative transfer capability for laboratory plasmas, J. Quant. Spectrosc. Radiat. Transfer **71**, 689 (2001).

[21] H.-K. Chung, M. H. Chen, W. L. Morgan, Y. Ralchenko, and R. W. Lee, FLYCHK: Generalized population kinetics and spectral model for rapid spectroscopic analysis for all elements, High Energy Density Phys. **1**, 3 (2005).

[22] P. Jönsson, G. Gaigalas, J. Bieroń, C. F. Fischer, and I. Grant, New version: GRASP2K relativistic atomic structure package, Comput. Phys. Commun. **184**, 2197 (2013).

[23] A. Schulze-Halberg, J. García-Ravelo, C. Pacheco-García, and J. J. P. Gil, A position-dependent mass model for the Thomas–Fermi potential: Exact solvability and relation to δ-doped semiconductors, Ann. Phys. (NY) **333**, 323 (2013).

[24] P. A. Doyle and P. S. Turner, Relativistic Hartree–Fock X-ray and electron scattering factors, Acta Cryst. A **24**, 390 (1968).

[25] I. Feranchuk and L. Komarov, The operator method of the approximate solution of the Schrödinger equation, Phys. Lett. A **88**, 211 (1982).

[26] I. Feranchuk, A. Ivanov, V.-H. Le, and A. Ulyanenkov, Non-perturbative description of quantum systems, *Lecture Notes in Physics* (Springer, Berlin, 2015).

[27] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, Phys. Rev. **136**, B864 (1964).

[28] L. Landau and E. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory* (Butterworth-Heinemann, Oxford, UK, 1977).

[29] E. Madelung, in *Die Mathematischen Hilfsmittel des Physikers*, edited by K. Boehle and S. Flügge (Springer Nature, Berlin, 1936).

[30] V. M. Klechkovskii, Justification of the rule for successive filling of $(n + l)$ groups, Zh. Eksp. Teor. Fiz. **41**, 465 (1962) [Sov. Phys. JETP **14**, 334 (1962)].

[31] J. J. Yeh and I. Lindau, Atomic subshell photoionization cross sections and asymmetry parameters: $1 \leqslant z \leqslant 103$, At. Data Nucl. Data Tables **32**, 1 (1985).

[32] M. Filatov, First principles calculation of Mössbauer isomer shift, Coord. Chem. Rev. **253**, 594 (2009).

[33] O. J. Heilmann and E. H. Lieb, Electron density near the nucleus of a large atom, Phys. Rev. A **52**, 3628 (1995).

[34] *International Tables for Crystallography*, Volume C: Mathematical, Physical and Chemical Tables, edited by E. Prince, 3rd ed. (International Union of Crystallography, Dordrecht, 2006).

[35] D. Waasmaier and A. Kirfel, New analytical scattering-factor functions for free atoms and ions, Acta Cryst. A **51**, 416 (1995).

[36] See Supplemental Material at http://link.aps.org/supplemental/10.1103/6lb9-p367 for additional derivations, numerical details, and supplemental figures.

[37] Q. S. Nguyen, Data for all figures, Zenodo (2025), https://doi.org/10.5281/zenodo.17611855.