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Atomic core-ionization energies; approximately piecewise-linear and linear relationships

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Abstract In the generalized Sturmian method, solutions to the many-particle Schrödinger equation are built up from isoenergetic sets of solutions to an approximate Schrödinger equation with a weighted potential $\beta_\nu V_0(\mathbf{x})$. The weighting factors β_ν are chosen in such a way as to make all of the members of the basis set correspond to the energy of the state being represented. In this paper we apply the method to core ionization in atoms and atomic ions, using a basis where $V_0(\mathbf{x})$ is chosen to be the nuclear attraction potential. We make use of a large-Z approximation, which leads to extremely simple closed-form expressions not only for energies, but also for values of the electronic potential at the nucleus. The method predicts approximately piece-wise linear dependence of the core-ionization energies on the number of electrons N for isonuclear series, and an approximately linear dependence of $\Delta E - Z^2/2$ on the nuclear charge Z for isoelectronic series.

Keywords Generalized Sturmians · Large-Z approximation · Atomic structure · Core-ionization · Electronic potential

1 Introduction

Because of their completeness properties, one-electron Sturmian basis sets have long been used in atomic physics. The members of such basis sets are isoenergetic solutions

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to an approximate Schrödinger equation with a weighted potential, the weighting factor being chosen so that all the members of the set correspond to the same energy. For example, Coulomb Sturmian basis sets are square-integrable isoenergetic sets of functions that obey

$$\left[-\frac{1}{2}\nabla^2 - \beta_n \frac{1}{r} - E \right] \phi_{nlm}(\mathbf{x}) = 0 \tag{1}$$

If the weighting factor β_n is chosen to be $\beta_n = kn$ for a positive k, then all the solutions correspond to the energy $E = -k^2/2$. In Eq. 1, and throughout this paper, atomic units are used, so that all energies are in Hartrees and all lengths in Bohrs.

In 1968, Goscinski [19] generalized the Sturmian concept by introducing basis sets that are solutions to an approximate many-particle Schrödinger equation with a weighted potential:

$$\left[-\sum_{j=1}^{N} \frac{1}{2m_j}\nabla_j^2 + \beta_\nu V(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) - E \right] \Phi_\nu(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = 0 \tag{2}$$

the weighting factor β_ν once again being chosen in such a way as to make all of the solutions correspond to the same energy. Basis sets of this kind can be used in a wide variety of problems.

In the present paper, Sect. 2–5 review the generalized Sturmian method as well as the large-Z approximation for atoms and ions that was introduced by us in [17]. These methods have been described in much more detail in our recent book [22]. Other work on Sturmians and generalized Sturmians can be found in references [2–21].

In the remainder of the paper, we apply the generalized Sturmian method in the large-Z approximation to atomic core ionization. The generalized Sturmian method in the large-Z approximation yields strikingly simple expressions for the electronic potential at the nuclei of atoms and atomic ions, as is shown in Sect. 6.

The method also yields extremely simple closed form expressions for the approximate energies of both the ground states and excited states of atoms and atomic ions. In Sect. 7, these closed form expressions are used to derive an approximate linear dependence of the core ionization energies of isoelectronic series on the nuclear charge Z, and an approximate piecewise linear dependence for isonuclear series on the number of electrons N. The expression for the potential at the nucleus gives insight into the piecewise linear core ionization energies of isonuclear series.

The accuracy of the large-Z approximation for few-electron systems is such that even for moderate values of Z, inaccuracies are much smaller than relativistic corrections. An approximate method for making relativistic corrections is introduced in Sect. 8. It is shown that the corrected energies rapidly approach the experimental ones as Z increases.

2 The generalized Sturmian method applied to atoms

In atomic units, the non-relativistic Schrödinger equation for an N-electron atom or atomic ion with nuclear charge Z is given by

$$\left[-\frac{1}{2}\Delta + \mathsf{V}(\mathbf{x}) - E_\kappa \right] \Psi_\kappa(\mathbf{x}) = 0 \tag{3}$$

where Ψ_κ is the κth electronic state with E_κ the corresponding energy,

$$\mathsf{V}(\mathbf{x}) = -\sum_{j=1}^{N} \frac{Z}{r_j} + \sum_{j>i}^{N} \sum_{i=1}^{N} \frac{1}{r_{ij}} \tag{4}$$

and

$$-\frac{1}{2}\Delta \equiv -\frac{1}{2} \sum_{j=1}^{3N} \frac{\partial^2}{\partial x_j^2} \tag{5}$$

The solution is usually built up from a superposition of basis functions

$$\Psi_\kappa(\mathbf{x}) = \sum_\nu \Phi_\nu(\mathbf{x}) B_{\nu\kappa} \tag{6}$$

In the generalized Sturmian method, these basis functions are chosen to be isoenergetic solutions to an approximate Schrödinger equation with a weighted potential [2–21]:

$$\left[-\frac{1}{2}\Delta + \beta_\nu \mathsf{V}_0(\mathbf{x}) - E_\kappa \right] \Phi_\nu(\mathbf{x}) = 0 \tag{7}$$

The weighting factors β_ν are especially chosen so that E_κ is the energy of the state to be represented. For few-electron atoms or atomic ions, it is convenient to let $\mathsf{V}_0(\mathbf{x})$ be the electrostatic attraction potential of the nucleus:

$$\mathsf{V}_0(\mathbf{x}) = -\sum_{j=1}^{N} \frac{Z}{r_j} \tag{8}$$

such that

$$\mathsf{V}(\mathbf{x}) = \mathsf{V}_0(\mathbf{x}) + \mathsf{V}'(\mathbf{x}) \ \text{ with } \ \mathsf{V}'(\mathbf{x}) = \sum_{j>i}^{N} \sum_{i=1}^{N} \frac{1}{r_{ij}} \tag{9}$$

With this choice of $\mathsf{V}_0(\mathbf{x})$, the weighting factors β_ν are determined automatically, and Eq. 7 is satisfied by Slater determinants of the form:

$$\Phi_\nu(\mathbf{x}) = |\chi_{\mu_1} \chi_{\mu_2} \cdots \chi_{\mu_N}| \tag{10}$$

where the χ_μ's are hydrogenlike spin-orbitals

$$\chi_{nlm,+1/2}(\mathbf{x}_j) = R_{nl}(r_j)Y_{lm}(\theta_j, \phi_j)\alpha(j)$$
$$\chi_{nlm,-1/2}(\mathbf{x}_j) = R_{nl}(r_j)Y_{lm}(\theta_j, \phi_j)\beta(j) \tag{11}$$

with the weighted charges ([22], Chap. 3):

$$Q_\nu = \beta_\nu Z = \frac{p_\kappa}{\mathcal{R}_\nu} \tag{12}$$

where

$$p_\kappa \equiv \sqrt{-2E_\kappa} \tag{13}$$

and

$$\mathcal{R}_\nu \equiv \sqrt{\frac{1}{n_1^2} + \frac{1}{n_2^2} + \cdots + \frac{1}{n_N^2}} \tag{14}$$

Here $n_1, n_2, \ldots, n_N$ represent the principal quantum numbers of the hydrogenlike spin-orbitals in the configuration Φ_ν. The energy E_κ will then be related to the weighted nuclear charges Q_ν by

$$E_\kappa = -\frac{p_\kappa^2}{2} = -\frac{1}{2}Q_\nu^2 \mathcal{R}_\nu^2 = -\left(\frac{Q_\nu^2}{2n_1^2} + \frac{Q_\nu^2}{2n_2^2} + \cdots + \frac{Q_\nu^2}{2n_N^2}\right) \tag{15}$$

Each of the hydrogenlike spin-orbitals obeys a one-electron Schrödinger equation of the form:

$$\left[-\frac{1}{2}\nabla_j^2 + \frac{Q_\nu^2}{2n^2} - \frac{Q_\nu}{r_j}\right]\chi_\mu(\mathbf{x_j}) = 0 \tag{16}$$

From Eq. 16 it follows that

$$\left[-\frac{1}{2}\sum_{j=1}^{N}\nabla_j^2\right]\Phi_\nu(\mathbf{x}) = \left[-\left(\frac{Q_\nu^2}{2n_1^2} + \frac{Q_\nu^2}{2n_2^2} + \cdots + \frac{Q_\nu^2}{2n_N^2}\right)\right.$$
$$\left. + \left(\frac{Q_\nu}{r_1} + \frac{Q_\nu}{r_2} + \cdots + \frac{Q_\nu}{r_N}\right)\right]\Phi_\nu(\mathbf{x})$$
$$= \left[E_\kappa - \beta_\nu V_0(\mathbf{x})\right]\Phi_\nu(\mathbf{x}) \tag{17}$$

from which it can be seen that Eq. 7 will indeed be satisfied by the configurations Φ_ν, provided that the effective nuclear charges Q_ν are chosen according to the rule given in Eqs. 12–14. We shall call such a set of isoenergetic solutions to (7) with $V_0(\mathbf{x})$ chosen

to be the nuclear attraction potential a set of "Goscinskian configurations" to honor Prof. Osvaldo Goscinski's important early contributions to the generalized Sturmian method [19].

3 Potential-weighted orthonormality relations

A set of Goscinskian configurations obey potential-weighted orthonormality relations. This can be seen as follows: by rearranging the terms in Eq. 7 we obtain:

$$\int d\tau \; \Phi_{\nu'}^*(\mathbf{x}) \left[\frac{1}{2}\Delta + E_\kappa \right] \Phi_\nu(\mathbf{x}) = \beta_\nu \int d\tau \; \Phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \Phi_\nu(\mathbf{x}) \tag{18}$$

and similarly

$$\int d\tau \; \Phi_\nu^*(\mathbf{x}) \left[\frac{1}{2}\Delta + E_\kappa \right] \Phi_{\nu'}(\mathbf{x}) = \beta_{\nu'} \int d\tau \; \Phi_\nu^*(\mathbf{x}) V_0(\mathbf{x}) \Phi_{\nu'}(\mathbf{x}) \tag{19}$$

Subtracting the complex conjugate of (19) from (18) and making use of the Hermiticity of the kinetic energy operator, we obtain

$$(\beta_\nu - \beta_{\nu'}) \int d\tau \; \Phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \Phi_\nu(\mathbf{x}) = 0 \tag{20}$$

from which it follows that

$$\int d\tau \; \Phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \Phi_\nu(\mathbf{x}) = 0 \quad \text{if} \quad \beta_{\nu'} \neq \beta_\nu \tag{21}$$

The hydrogenlike spin orbitals are orthonormal:

$$\int d\tau_j \; \chi_{\mu'}^*(\mathbf{x}_j) \chi_\mu(\mathbf{x}_j) = \delta_{\mu'\mu} \tag{22}$$

and they obey the Virial Theorem:

$$-\int d\tau_j \; |\chi_\mu(\mathbf{x}_j)|^2 \frac{Q_\nu}{r_j} = -\frac{Q_\nu^2}{n^2} \tag{23}$$

Therefore, using first the Slater–Condon rules, then (12) and (23),

$$\int d\tau \; V_0(\mathbf{x}) |\Phi_\nu(\mathbf{x})|^2 = -\sum_{\mu \in \nu} \int d\tau_j \; |\chi_\mu(\mathbf{x}_j)|^2 \frac{Z}{r_j}$$

$$= -\frac{1}{\beta_\nu} \sum_{\mu \in \nu} \int d\tau_j \; |\chi_\mu(\mathbf{x}_j)|^2 \frac{Q_\nu}{r_j}$$

$$= -\frac{Q_\nu^2}{\beta_\nu} \sum_{\mu \in \nu} \frac{1}{n^2} = \frac{2E_\kappa}{\beta_\nu} \tag{24}$$

and thus we finally obtain the potential-weighted orthonormality relation:

$$\int d\tau \ \Phi_{\nu'}^*(\mathbf{x}) \mathsf{V}_0(\mathbf{x}) \Phi_\nu(\mathbf{x}) = \delta_{\nu'\nu} \frac{2E_\kappa}{\beta_\nu} = -\delta_{\nu'\nu} \frac{p_\kappa^2}{\beta_\nu} \tag{25}$$

4 Generalized Sturmian secular equations

We now introduce the definitions

$$T_{\nu'\nu}^0 \equiv -\frac{1}{p_\kappa} \int d\tau \ \Phi_{\nu'}^*(\mathbf{x}) \mathsf{V}_0(\mathbf{x}) \Phi_\nu(\mathbf{x}) \tag{26}$$

and

$$T_{\nu'\nu}' \equiv -\frac{1}{p_\kappa} \int d\tau \ \Phi_{\nu'}^*(\mathbf{x}) \mathsf{V}'(\mathbf{x}) \Phi_\nu(\mathbf{x}) \tag{27}$$

From the potential-weighted orthonormality relations (25) and the definition of β_ν (12) it follows that

$$T_{\nu'\nu}^0 = \delta_{\nu'\nu} Z\mathcal{R}_\nu \tag{28}$$

Thus the matrix $T_{\nu'\nu}^0$ is diagonal and independent of p_κ. It can be shown ([22], Appendix A) that $T_{\nu'\nu}'$ is also independent of p_κ, although it is not diagonal. We shall call $T_{\nu'\nu}'$ the "energy-independent interelectron repulsion matrix". To obtain the generalized Sturmian secular equations, we begin by substituting the superposition (6) into the Schrödinger equation (3). This yields:

$$\sum_\nu \left[-\frac{1}{2}\Delta + \mathsf{V}(\mathbf{x}) - E_\kappa \right] \Phi_\nu(\mathbf{x}) B_{\nu\kappa} = 0 \tag{29}$$

Next, we notice that since all of the isoenergetic Goscinskian configurations in the basis set obey (7), Eq. 29 can be rewritten as

$$\sum_\nu \left[\mathsf{V}(\mathbf{x}) - \beta_\nu \mathsf{V}_0(\mathbf{x}) \right] \Phi_\nu(\mathbf{x}) B_{\nu\kappa} = 0 \tag{30}$$

We then multiply by a conjugate function from our basis set and integrate over all space and spin coordinates:

$$\sum_\nu \int d\tau \ \Phi_{\nu'}^*(\mathbf{x}) \left[\mathsf{V}(\mathbf{x}) - \beta_\nu \mathsf{V}_0(\mathbf{x}) \right] \Phi_\nu(\mathbf{x}) B_{\nu\kappa} = 0 \tag{31}$$

Making use of Eqs. 26–28, we obtain

$$\sum_\nu \left[-p_\kappa \delta_{\nu'\nu} Z\mathcal{R}_\nu - p_\kappa T_{\nu'\nu}' + \beta_\nu p_\kappa \delta_{\nu'\nu} Z\mathcal{R}_\nu \right] B_{\nu\kappa} = 0 \tag{32}$$

Finally, using the relationship

$$\beta_\nu Z \mathcal{R}_\nu = p_\kappa \tag{33}$$

and dividing by p_κ, we obtain the generalized Sturmian secular equations:

$$\sum_\nu \left[\delta_{\nu'\nu} Z \mathcal{R}_\nu + T'_{\nu'\nu} - p_\kappa \delta_{\nu'\nu} \right] B_{\nu\kappa} = 0 \tag{34}$$

Equation 34 differs in several respects from the conventional secular equations used in quantum theory:

1. The kinetic energy term has vanished.
2. The nuclear attraction matrix is diagonal and energy-independent.
3. The interelectron repulsion matrix is energy-independent.
4. The roots are not energies but values of the *scaling parameter*, p_κ, which is proportional to the square roots of the binding energies (Eq. 13).
5. Before the secular equation is solved, only the form of the basis set is known, but not the values of the scaling parameters p_κ. Solution of the secular equations yields a near-optimum basis set appropriate for each state, as well as the states themselves and their corresponding energies.

5 The large-Z approximation: restriction of the basis set to an $\mathcal{R}$-block

If interelectron repulsion is entirely neglected, i.e. when disregarding the second term in Eq. 34, the calculated energies E_κ of Ψ_κ become those of a set of N completely independent electrons moving in the field of the bare nucleus:

$$E_\kappa = -\frac{p_\kappa^2}{2} \longrightarrow -\frac{1}{2} Z^2 \mathcal{R}_\nu{}^2 = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2} - \cdots - \frac{Z^2}{2n_N^2} \tag{35}$$

Equation 35 is not the large-Z approximation: in the large-Z approximation, we do not neglect interelectron repulsion, but we restrict the basis set to those Goscinskian configurations that would be degenerate if interelectron repulsion were entirely neglected, i.e., we restrict the basis to a set of configurations all of which correspond to the same value of $\mathcal{R}_\nu$. In that case, the first term in (34) is a multiple of the identity matrix, and the eigenvectors $B_{\nu\kappa}$ are the same as those that would be obtained by diagonalizing the energy-independent interelectron repulsion matrix $T'_{\nu'\nu}$, since the eigenfunctions of any matrix are unchanged by adding a multiple of the unit matrix.

$$\sum_\nu \left[T'_{\nu'\nu} - \lambda_\kappa \delta_{\nu'\nu} \right] B_{\nu\kappa} = 0 \tag{36}$$

The roots are shifted by an amount equal to the constant by which the identity matrix is multiplied:

$$p_\kappa = Z \mathcal{R}_\nu + \lambda_\kappa = Z \mathcal{R}_\nu - |\lambda_\kappa| \tag{37}$$

and the energies become

$$E_\kappa = -\frac{1}{2}(Z\mathcal{R}_\nu - |\lambda_\kappa|)^2 \tag{38}$$

Since the roots λ_κ are always negative, we may use the form $-|\lambda_\kappa|$ in place of λ_κ to make explicit the fact that interelectron repulsion reduces the binding energies, as of course it must. The roots λ_κ are pure numbers that can be calculated once and for all and stored. From these roots, a great deal of information about atomic states can be found with very little effort.

6 Electronic potential at the nucleus

The electronic potential $\varphi(\mathbf{x}_1)$ is related to the electronic density distribution by

$$\varphi(\mathbf{x}_1) = \int d^3x_1' \frac{\rho(\mathbf{x}_1')}{|\mathbf{x}_1 - \mathbf{x}_1'|} \tag{39}$$

If the coordinate system is centered on the nucleus, the electronic potential at the nucleus is then given by

$$\varphi(0) = \int d^3x_1' \frac{\rho(\mathbf{x}_1')}{|\mathbf{x}_1'|} \tag{40}$$

But the electron density corresponding to the state Ψ_κ is defined as

$$\rho(\mathbf{x}_1) = N \int ds_1 \int d\tau_2 \int d\tau_3 \ldots \int d\tau_N \Psi_\kappa^*(\mathbf{x})\Psi_\kappa(\mathbf{x}) \tag{41}$$

where the integral is taken over the spin coordinate of the first electron and over the space and spin coordinates of all the other electrons. The wave function $\Psi_\kappa(\mathbf{x}) = \sum_\nu \Phi_\kappa(\mathbf{x})B_{\nu\kappa}$ is a linear combination of Goscinskian configurations. Thus the density is given by

$$\rho(\mathbf{x}_1) = \sum_{\nu',\nu} \rho_{\nu'\nu}(\mathbf{x}_1) B_{\nu\kappa}^* B_{\nu\kappa} \tag{42}$$

where

$$\rho_{\nu'\nu}(\mathbf{x}_1) = N \int ds_1 \int d\tau_2 \cdots \int d\tau_N \Phi_{\nu'}^*(\mathbf{x})\Phi_\nu(\mathbf{x})$$

$$= \begin{cases} 0 & \text{for} \quad |\nu' \setminus \nu| \geq 2 \\ \chi_{\mu'}^*(\mathbf{x}_1)\chi_\mu(\mathbf{x}_1) & \text{for} \quad \nu' \setminus \nu = \{\mu\} \text{ and } \nu \setminus \nu' = \{\mu'\} \\ \sum_{i=1}^N |\chi_{\mu_i}(\mathbf{x}_1)|^2 & \text{for} \quad \nu' = \nu \end{cases} \tag{43}$$
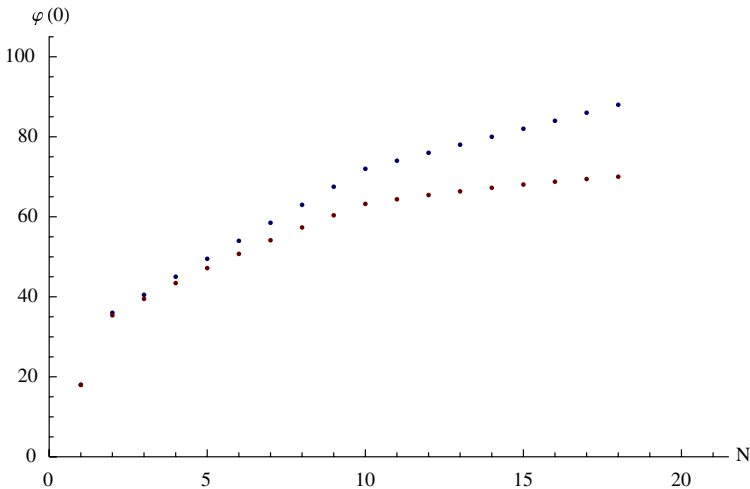
Fig. 1 The electronic potentials at the nuclei of ions in the isonuclear series with nuclear charge $Z = 18$ are shown for $1 \leq N \leq 18$. The upper set of dots were generated neglecting interelectron repulsion, and are seen to be exactly piecewise linear. The lower set of values take interelectron repulsion into account

In Eq. 43 we have made use of the fact that within an $\mathcal{R}$-block, the atomic spin-orbitals are orthonormal.

We calculated the potential at the nucleus (within the framework of the large-Z approximation) by generating the wave functions and from those the densities, using Eqs. 40–43. By this somewhat laborious method, we obtained the values shown in Fig. 1. In this figure, the upper dots correspond to densities generated neglecting interelectron repulsion. In the lower set of dots, interelectron repulsion is included. The fact that the unscreened values were exactly piecewise linear, and that the more exact values that included repulsion were very nearly piecewise linear, was so striking, that we were challenged to explain it.

In finding the explanation we were led to surprisingly simple expressions for the potential at the nucleus of an atom or ion: within the framework of the large-Z approximation we have

$$
\int d\tau \, \Psi_\kappa^*(\mathbf{x}) V_0(\mathbf{x}) \Psi_\kappa(\mathbf{x}) = \sum_{\nu'} \sum_{\nu} B_{\nu'\kappa}^* B_{\nu\kappa} \int d\tau \, \Phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \Phi_\nu(\mathbf{x})
$$

$$
= -\frac{p_\kappa^2}{\beta_\nu} \sum_\nu |B_{\nu\kappa}|^2 \tag{44}
$$

In the second step above, we make use of the potential weighted orthonormality relation (25). Further, since $\sum_\nu |B_{\nu\kappa}|^2 = 1$, Eq. 44 reduces to

$$
\int d\tau \, \Psi_\kappa^*(\mathbf{x}) V_0(\mathbf{x}) \Psi_\kappa(\mathbf{x}) = -\frac{p_\kappa^2}{\beta_\nu} = -p_\kappa Z \mathcal{R}_\nu \tag{45}
$$

This result can be used to express the electronic potential at the nucleus in a very simple form. Combining (40) and (41), we obtain

$$\varphi(0) = N \int d\tau \frac{1}{|\mathbf{x}_1|} \Psi_\kappa^*(\mathbf{x}) \Psi_\kappa(\mathbf{x}) \tag{46}$$

From the definition of V_0, (8), and from the fact that each term in the sum in (8) gives the same contribution, we have

$$\varphi(0) = -\frac{1}{Z} \int d\tau \Psi_\kappa^*(\mathbf{x}) \mathsf{V}_0(\mathbf{x}) \Psi_\kappa(\mathbf{x}) \tag{47}$$

Combining Eqs. 45 and 47 we obtain the extremely simple result:

$$\varphi(0) = p_\kappa \mathcal{R}_\nu \tag{48}$$

which can alternatively be written in the form:

$$\varphi(0) = Z\mathcal{R}_\nu{}^2 - |\lambda_\kappa|\mathcal{R}_\nu \tag{49}$$

or in a third form:

$$\varphi(0) = Q_\nu \mathcal{R}_\nu{}^2 \tag{50}$$

since $Q_\nu = Z - |\lambda_\kappa|/\mathcal{R}_\nu$. From Eqs. 48–50 it follows that for an isonuclear series, the electronic potential at the nucleus depends on N in an approximately piecewise linear way. For example, let us consider the isonuclear series where $Z = 18$. Keeping the nuclear charge Z constant at this value, we begin to add electrons. For the ground state we have:

$$\mathcal{R}_\nu{}^2 \equiv \frac{1}{n_1^2} + \frac{1}{n_2^2} + \cdots + \frac{1}{n_N^2} = \begin{cases} \frac{N}{1} & N \leq 2 \\ \frac{2}{1} + \frac{N-2}{4} & 2 \leq N \leq 10 \\ \frac{2}{1} + \frac{8}{4} + \frac{N-10}{9} & 10 \leq N \leq 18 \end{cases} \tag{51}$$

Tables 1–3 show the roots $|\lambda_\kappa|$ of the energy-independent interelectron repulsion matrix $T'_{\nu'\nu}$. For each value of N, the numerically smallest of these roots corresponds to the ground state. The term $Z\mathcal{R}_\nu{}^2$ is dominant in Eq. 49. When the second term is entirely neglected, i.e., when the effects of interelectron repulsion are neglected, then the dependence of $\varphi(0)$ on N is exactly piecewise linear. However, because of the presence of the second term, the N-dependence is only approximately piecewise linear.

Table 1 Roots of the ground state $\mathcal{R}$-block of the interelectron repulsion matrix for the He-like, Li-like, Be-like, B-like and C-like isoelectronic series

He-like $|\lambda_K|$	Term	Li-like $|\lambda_K|$	Term	Be-like $|\lambda_K|$	Term	B-like $|\lambda_K|$	Term	C-like $|\lambda_K|$	Term
0.441942	^{1}S	0.681870	^{2}S	0.986172	^{1}S	1.40355	^{2}P	1.88151	^{3}P
		0.729017	^{2}P	1.02720	^{3}P	1.44095	^{4}P	1.89369	^{1}D
				1.06426	^{1}P	1.47134	^{2}D	1.90681	^{1}S
				1.09169	^{3}P	1.49042	^{2}S	1.91623	^{5}S
				1.10503	^{1}D	1.49395	^{2}P	1.995141	^{3}D
				1.13246	^{1}S	1.52129	^{4}S	1.96359	^{3}P
						1.54037	^{2}D	1.98389	^{3}S
						1.55726	^{2}P	1.98524	^{1}D
								1.99742	^{1}P
								2.04342	^{3}P
								2.05560	^{1}D
								2.07900	^{1}S

Table 2 Roots of the ground state $\mathcal{R}$-block of the interelectron repulsion matrix $T'_{v'v}$ for the N-like, O-like, F-like and Ne-like isoelectronic series

N-like $|\lambda_K|$	Term	O-like $|\lambda_K|$	Term	F-like $|\lambda_K|$	Term	Ne-like $|\lambda_K|$	Term
2.41491	^{4}S	3.02641	^{3}P	3.68415	^{2}P	4.38541	^{1}S
2.43246	^{2}D	3.03769	^{1}D	3.78926	^{2}S		
2.44111	^{2}P	3.05065	^{1}S				
2.49314	^{4}P	3.11850	^{3}P				
2.52109	^{2}D	3.14982	^{1}P				
2.53864	^{2}S	3.24065	^{1}S				
2.54189	^{2}P						
2.61775	^{2}P						

In Fig. 2, we see that the values for the electronic potential at the nucleus, laboriously calculated by generating wave functions and densities, are exactly duplicated by the simple expressions in Eqs. 48–50, as well as (51) when interelectron repulsion is neglected.

We should remember that Eqs. 48–50 were derived within the framework of the large-Z approximation. Thus the piecewise-linear dependence of $\varphi(0)$ on N is only an approximate one for two reasons—firstly because the term $-|\lambda_K|\mathcal{R}_v$ is slightly nonlinear, and secondly because of the inaccuracies inherent in the large-Z approximation.

Table 3 Numerically smallest roots of the $\mathcal{R}$-blocks and $\mathcal{R}_\nu'$-blocks of the interelectron repulsion matrix $T'_{\nu'\nu}$, where $2 \leq N \leq 14$, and where $N' = N - 1$ is the number of electrons remaining after core ionization. Primed quantities refer to the core-ionized states

| N	$\mathcal{R}_\nu$	$|\lambda_\kappa|$	Term	N'	$\mathcal{R}_\nu'$	$|\lambda_\kappa'|$	Term
2	$\sqrt{8}/2$	0.441942	^{1}S	1	$\sqrt{4}/2$	0.000000	^{2}S
3	$\sqrt{9}/2$	0.681870	^{2}S	2	$\sqrt{5}/2$	0.168089	^{3}S
4	$\sqrt{10}/2$	0.986172	^{1}S	3	$\sqrt{6}/2$	0.433936	^{2}S
5	$\sqrt{11}/2$	1.40355	^{2}P	4	$\sqrt{7}/2$	0.800757	^{3}P
6	$\sqrt{12}/2$	1.88151	^{3}P	5	$\sqrt{8}/2$	1.23703	^{4}P
7	$\sqrt{13}/2$	2.41491	^{4}S	6	$\sqrt{9}/2$	1.73489	^{5}S
8	$\sqrt{14}/2$	3.02641	^{3}P	7	$\sqrt{10}/2$	2.33058	^{4}P
9	$\sqrt{15}/2$	3.68415	^{2}P	8	$\sqrt{11}/2$	2.97391	^{3}P
10	$\sqrt{16}/2$	4.38541	^{1}S	9	$\sqrt{12}/2$	3.66181	^{2}S
11	$\sqrt{37}/3$	4.75240	^{2}S	10	$\sqrt{28}/3$	4.02987	^{3}S
12	$\sqrt{38}/3$	5.1410	^{1}S	11	$\sqrt{29}/3$	4.4243	^{2}S
13	$\sqrt{39}/3$	5.5860	^{2}P	12	$\sqrt{30}/3$	4.8733	^{3}P
14	$\sqrt{40}/3$	6.0512	^{3}P	13	$\sqrt{31}/3$	5.3434	^{4}P
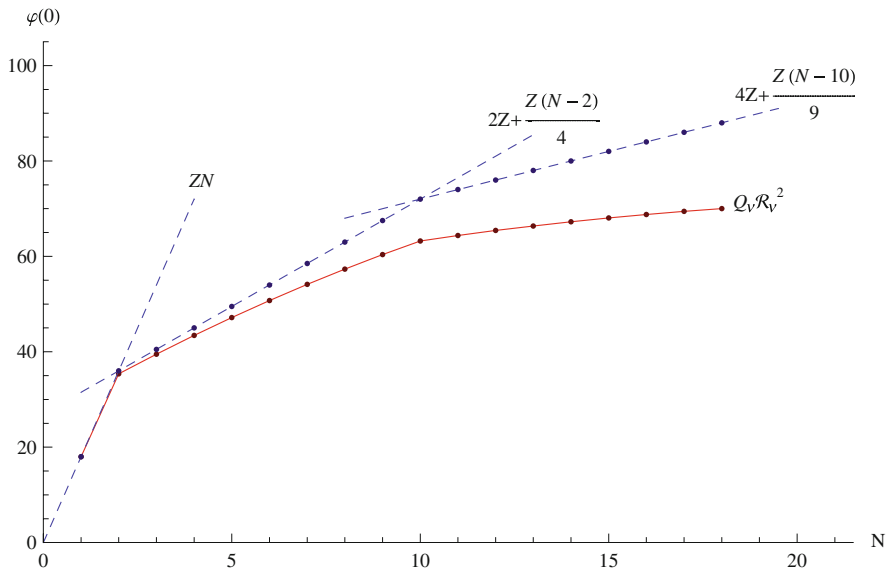
Fig. 2 When interelectron repulsion is entirely neglected, the electronic potential at the nucleus is given by $Z\mathcal{R}_\nu^2$, which is exactly piecewise linear in N. The effect of interelectron repulsion is to decrease $\varphi(0)$ and to make the dependence only approximately piecewise linear. The figure shows $\varphi(0)$ neglecting interelectron repulsion (upper values) and including it (lower values). The dots are calculated from the electronic densities of the ground state wave functions, whereas the lines are the closed form expressions found in Eqs. 49 and 51

7 Core ionization energies

The large-Z approximation can be used to calculate core-ionization energies, i.e., the energies required to remove an electron from the inner shell of an atom. From (38) we can see that this energy will be given by

$$\Delta E = \frac{1}{2}\left[(Z\mathcal{R}_\nu - |\lambda_\kappa|)^2 - (Z\mathcal{R}_\nu{}' - |\lambda_\kappa'|)^2\right] \tag{52}$$

where the unprimed quantities refer to the original ground state, while the primed quantities refer to the core-ionized states (Table 2). Since

$$\mathcal{R}_\nu{}^2 - \mathcal{R}_\nu{}'^2 = 1 \tag{53}$$

Equation 52 can be written in the form

$$\Delta E - \frac{Z^2}{2} = Z\left[\mathcal{R}_\nu{}'|\lambda_\kappa'| - \mathcal{R}_\nu|\lambda_\kappa|\right] + \frac{|\lambda_\kappa|^2 - |\lambda_\kappa'|^2}{2} \tag{54}$$

Thus we can see that within the framework of the large-Z approximation, the quantity $\Delta E - Z^2/2$ is linear in Z for an isoelectronic series (Table 3). This quantity represents the contribution of interelectron repulsion to the core ionization energy, since if interelectron repulsion is completely neglected, the core ionization energy is given by $\Delta E = Z^2/2$. Core ionization energies calculated from Eqs. 52–54 are shown in Figs. 3–5.
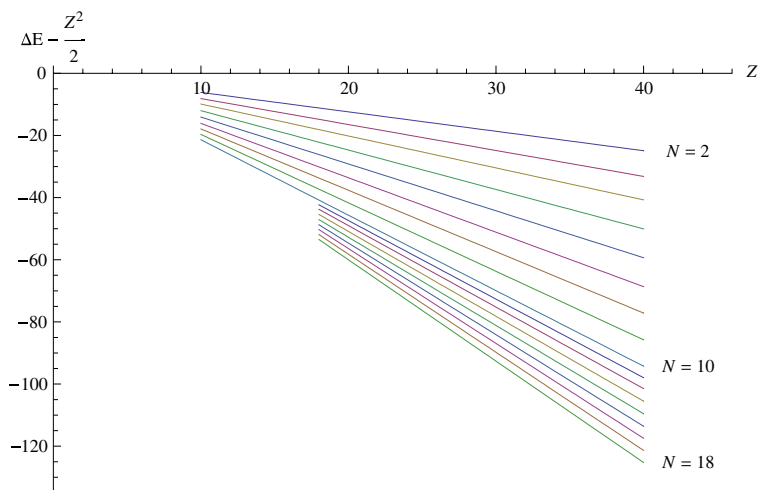

Fig. 3 For isoelectronic series, Eq. 54 indicates that within the large-Z approximation, the quantity $\Delta E - Z^2/2$ is exactly linear in Z, as is illustrated above
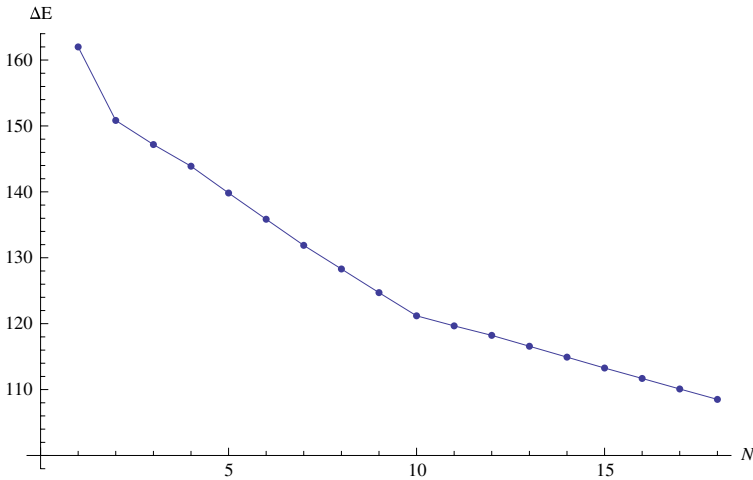
Fig. 4 For isonuclear series, the dependence on N is approximately piecewise linear. Whenever a new shell starts to fill, the slope of the line changes. The dots in the figure were calculated using Eq. 54, where it is not obvious that the dependence ought to be approximately piecewise linear. However, Eqs. 49 and 51 can give us some insight into the approximately piecewise linear relationship
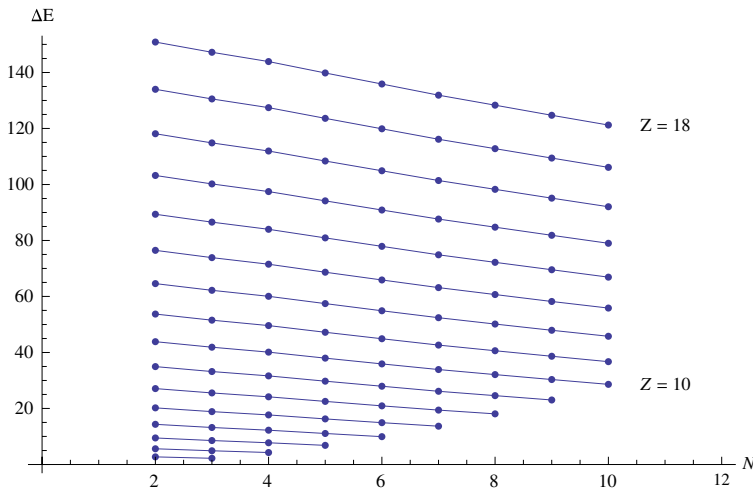

Fig. 5 This figure shows the dependence of the core-ionization energy on both N and Z for the filling of the $n = 2$ shell

8 Validity of the large-Z approximation

In Fig. 6, the large-Z approximation $E_\kappa = -\frac{1}{2}(Z\mathcal{R}_\nu - |\lambda_\kappa|)^2$ for the lowest triplet states of the helium-like isoelectronic series is plotted against spectroscopically determined energies. In order to better see the details, we plot E_κ/Z^2 in Fig. 7. Figure 8 shows E_κ/Z^2 for the ground state of the six-electron isoelectronic series.
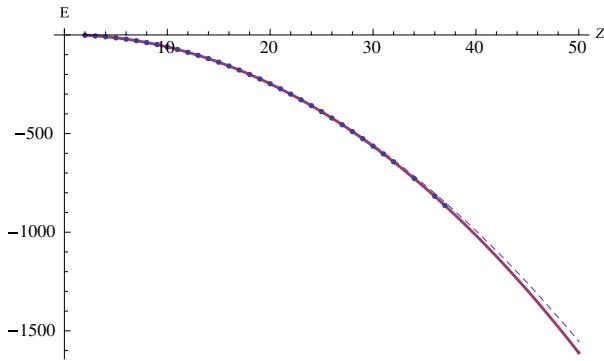
Fig. 6 Energies for the lowest ^{3}S state of the helium-like isoelectronic series calculated in the large-Z approximation, which here limits the basis to a single configuration. The lower (solid) line is corrected for relativistic effects as discussed in the text; the dots indicate experimental values from the NIST tables
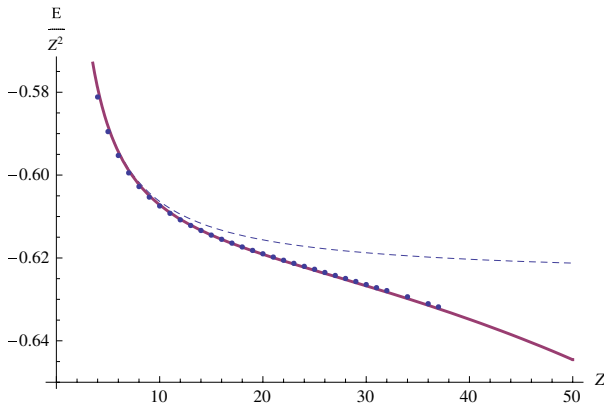

Fig. 7 Here the ^{3}S energies shown in Fig. 6 are divided by Z^2. The lower line is corrected for relativistic effects. The dots are experimental values
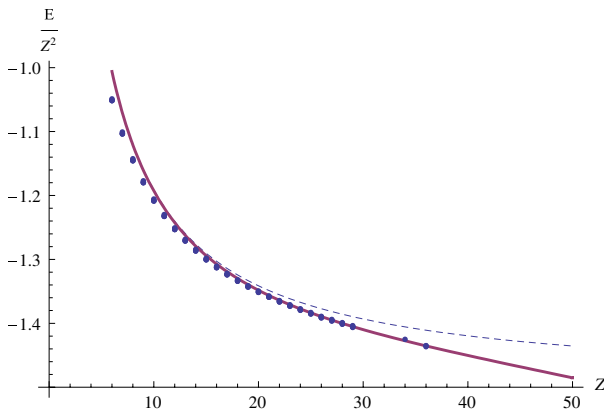

Fig. 8 The ground state of the carbon-like isoelectronic series

As the nuclear charge Z increases, the energies and wave functions calculated with the large-Z approximation approach the exact solutions to the non-relativistic Schrödinger equation. However, relativistic effects begin to be pronounced at around $Z = 10$, and become progressively more so as Z increases. Therefore the calculated values first approach the experimental ones, but begin to differ as relativity becomes more and more important.

It is possible to make a rough correction for the relativistic effect on the energies by multiplying them by an easily calculated factor $f_\kappa(Z)$, so that E_κ becomes

$$-\frac{1}{2} f_\kappa(Z)(Z\mathcal{R}_\nu + \lambda_\kappa)^2 \tag{55}$$

The correction factor $f_\kappa(Z)$ is the ratio between the relativistic and non-relativistic energies of a configuration, assuming interelectron repulsion to be completely neglected such that the energy is equal to that of N independent electrons moving in the field of the nucleus.

In the nonrelativistic case, the energy of a hydrogenlike spin-orbital is given by $-\frac{Z^2}{2n^2}$, and thus the total energy of an N-electron configuration is $-\frac{1}{2}Z^2\mathcal{R}_\nu{}^2$.

In the relativistic case, the energy of a single electron in a hydrogenlike orbital can be found, for example, in [1], or in [22], Eqs. 7.35 through 7.40.

We wish to compare these two energies E_{rel} and E_{nonrel} for a multiconfigurational state

$$\Psi_\kappa = \sum_\nu \Phi_\nu B_{\nu\kappa} \tag{56}$$

the ratio being

$$f_\kappa(Z) = \frac{E_{\mathrm{rel}}}{E_{\mathrm{nonrel}}} = \frac{\sum_\nu B_{\nu\kappa}^2 \langle \Phi_\nu | \mathsf{H}_0 | \Phi_\nu \rangle_{\mathrm{rel}}}{\sum_\nu B_{\nu\kappa}^2 \langle \Phi_\nu | \mathsf{H}_0 | \Phi_\nu \rangle_{\mathrm{nonrel}}} = \frac{\sum_\nu B_{\nu\kappa}^2 \langle \Phi_\nu | \mathsf{H}_0 | \Phi_\nu \rangle_{\mathrm{rel}}}{-\frac{1}{2}Z^2 \sum_\nu B_{\nu\kappa}^2 \mathcal{R}_\nu{}^2} \tag{57}$$

Here, H_0 is a sum of one-electron Hamiltonian operators corresponding to single electrons moving in the field of the bare nucleus, i.e. interelectron repulsion is completely neglected.

In the figures, the lines are calculated in the large-Z approximation. The upper (dashed) line is not corrected for relativistic effects, while the lower (solid) line is corrected. The dots are experimental values of the energies taken from the NIST Atomic Spectra Database [24]. It can be seen from Figs. 5–7 that agreement between the energies calculated from the large-Z approximation and experimental energies become progressively better as Z increases, provided that the rough relativistic correction is made.

We note that the large-Z approximation, despite it's great simplicity, well approximates non-relativistic energies; even for modest values of nuclear charge, the error of the large-Z approximation is smaller than the error due to neglecting relativity. Further, relativistic effects may be accounted for by means of an easily calculated factor, yielding energies that correspond well with experiment.

The second example presented here (the ground state of the carbonlike isoelectronic series) is a case not easily approximated using a small number of Goscinskian basis functions, because interelectron repulsion plays a large role. Nevertheless, it can be seen that even in this somewhat difficult case, the large-Z approximation gives very reasonable results. The large-Z approximation is not only extremely simple, but it is characterized by a small number of parameters–the roots of the interelectron repulsion matrix. These roots are dimensionless and independent of energy and of nuclear charge. They can be calculated once and for all, and they contain information concerning many states of the entire isoelectronic series. Once the roots are obtained, calculating approximate atomic energies, and a number of other properties, become tasks that can be performed on the back of an envelope.

9 Discussion

It can be seen that the core ionization energies predicted from the large-Z approximation depend on N in an approximately piecewise-linear way for isonuclear series, while $\Delta E - Z^2/2$ depends linearly on Z for isoelectronic series. This result is made plausible by Eqs. 48–51, in which the electronic potential at the nucleus is shown to depend approximately piecewise-linearly on N for isonuclear series and linearly on Z for isoelectronic series. It can also be seen that the generalized Sturmian method using Goscinskian configurations provides us with a powerful and convenient method for understanding the properties of atoms and atomic ions. In the large-Z approximation, the method leads to extremely simple closed-form expressions, not only for energies, but also for the behavior of the electronic potential near to the nucleus.

The programs used for the calculations in this paper can be downloaded from: http://sturmian.kvante.org/papers/linear.

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