

Effective-Charge Coordinate $Q(Z)$ for the Periodic Law: Cardano–Newton Analytic Inversion, Kantorovich Bounds, Isoelectronic Extension, and Fourier Decomposition

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Abstract

We construct and rigorously analyse a real-analytic periodic-law coordinate Q : $[0, \infty) \rightarrow \mathbb{R}$ built from the smooth extension of the Hakala (1952) formula for the atomic number of the noble gas closing period P . Setting the trigonometric correction to zero yields a cubic solved by the Cardano formula for a zeroth-order approximation $Q_0(Z)$; one Newton step provides a closed-form correction $Q_1(Z)$. We prove existence, uniqueness and real-analyticity of Q_0 on the physical domain, axiomatic uniqueness of the chosen smooth extension within a minimal ansatz, certified Newton convergence bounds, and a refined asymptotic expansion consistent at leading order with the Thomas-Fermi-Tietz limit. Empirically, Q restores periodic alignment for several tabulated properties but is not by itself a universal predictor. A structured Q model combining trend(Q), circular functions of frac Q , and MJK orbital variables substantially improves leave-one-period-out prediction for IP_1 , chi, r_{cov} , and r_{vdW} , and improves the $Z \leq 86 \rightarrow 87 - 118$ extrapolation for IP_1 and radii. An MJK-only ablation (Table 8) further shows that the added value of Q itself, over the MJK combinatorial features alone, is concentrated on IP_1 and the radii — most clearly on

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r_{cov} — while for χ , T_m and EA the improvement is largely inherited from the MJK variables. Electron affinity remains the weakest property and is reported separately as a data-quality-sensitive endpoint. A rank comparison with the Pettifor chemical scale indicates complementary rather than interchangeable ordering.

1 Introduction

The Madelung–Janet–Klechkovskii (MJK) rule for orbital filling — increasing $n + \ell$, ties broken by increasing n — provides a highly accurate combinatorial framework for the electronic ground states of neutral atoms [1, 22, 27]. In 1952 Hakala [10] derived a closed-form polynomial relation between the atomic number Z , the quantum numbers (n, ℓ) and the sub-shell electron count N :

$$Z = \frac{(n + \ell)(n + \ell + 1)(n + \ell + 2)}{6} + \frac{(n + \ell + 1)[1 - (-1)^{n+\ell}]}{4} - 2(\ell + 1)^2 + N, \quad (1.1)$$

with the Cardano-form inversion given in footnote 10 of that paper. Klechkovskii’s monograph [18] systematized this result and Weise [40] recast the noble-gas formula in a Pythagorean-inspired closed form. Belokolos [3] proved that the same expressions arise from Bohr–Sommerfeld quantization of the Tietz rational approximation to the Thomas–Fermi atomic potential. Related group-theoretical, topological and information-theoretic formulations of the periodic system have been developed [4, 9, 15, 16, 32, 34].

A recent preprint by Schumacher [37] observed that replacing $(-1)^M$ in (1.1) by $\cos \pi M$ yields a real-analytic function of the continuous variable M , opening the way for Newton-type root-finding on the smooth extension. The present work develops the mathematical theory of the resulting periodic-law coordinate $Q(Z)$, proves rigorous existence, uniqueness and convergence theorems, extends the construction to ionic species via a two-parameter family $Q_{\text{iso}}(Z, N)$, and reports extensive empirical validation. Our original contributions are:

(i) Existence and real-analyticity of the Cardano root Q_0 on the positive real axis (Theorem 3.1).

(ii) Closed-form expression of the Newton correction Q_1 (Theorem 3.2) and explicit Newton–Kantorovich convergence bounds verifying Kantorovich constant $h < \frac{1}{2}$ at every noble gas (Theorem 3.4).

(iii) Axiomatic uniqueness of the smooth extension R_g among polynomial-plus-trigonometric ansatz functions (Theorem 3.5).

(iv) Refined asymptotic expansion of $M_0(Z)$ up to order $O(Z^{-7/3})$, coinciding at leading order with the Thomas–Fermi–Tietz result of Belokolos (Theorem 4.1).

(v) A two-parameter isoelectronic extension $Q_{\text{iso}}(Z, N)$ and the isoelectronic invariance principle for sequential ionization potentials (§6, Proposition 6.1).

(vi) Fourier decomposition, Bochner-style autocorrelation, continuous wavelet transform, and bootstrap cross-spectral coherence analysis of the periodic shape curves (§5, Propositions 5.1–5.3).

(vii) Riemann-surface characterisation of $Q_0(z)$ identifying $z_c^- = -2 - \frac{1}{9\sqrt{3}}$ as the sole singularity of the physical branch and $z_c^+ = -2 + \frac{1}{9\sqrt{3}}$ as a Puiseux branch point of only the other two sheets (Theorem 3.6). Both lie outside the physical domain $z \geq 0$.

(viii) Bootstrap and period-aware empirical validation, comparison with Pettifor, Mendeleev, and pymatgen-ridge composition baselines, and a Q-structured predictive model tested by leave-one-period-out and forward interval holdouts (§§7–9).

2 Preliminaries and notation

Let $\mathbb{N} = \{1, 2, 3, \dots\}$ and $\mathbb{Z}_{\geq 0} = \{0, 1, 2, \dots\}$. For a real-analytic function $f: I \rightarrow \mathbb{R}$ on an open interval $I \subset \mathbb{R}$, we denote its k -th derivative by $f^{(k)}$.

Let $M = n + \ell$, the Madelung number of a sub-shell (n, ℓ) with $0 \leq \ell \leq n - 1$. Summing the capacity $2(2\ell + 1)$ of each sub-shell up to M gives the total electron count in the first M shells:

$$N_M^{\max} = \frac{M(M+1)(M+2)}{6} + \frac{(M+1)[1 - (-1)^M]}{4}, \quad M \in \mathbb{N}. \quad (2.1)$$

The atomic number of the noble gas closing period P is

$$Rg_{\text{disc}}(P) = \frac{(P+1)(P+2)(P+3)}{6} + \frac{(P+2)[1 + (-1)^P]}{4} - 2, \quad P \in \mathbb{N}, \quad (2.2)$$

yielding $Rg_{\text{disc}}(1) = 2$ (He), $Rg_{\text{disc}}(2) = 10$ (Ne), $\dots$, $Rg_{\text{disc}}(7) = 118$ (Og).

Definition 2.1 (smooth extension Rg).

The real-analytic extension $Rg: \mathbb{R} \rightarrow \mathbb{R}$ of (2.2) is defined by

$$Rg(Q) := \frac{(Q+1)(Q+2)(Q+3)}{6} + \frac{(Q+2)[1 + \cos \pi Q]}{4} - 2, \quad Q \in \mathbb{R}. \quad (2.3)$$

By elementary trigonometry $Rg(k) = Rg_{\text{disc}}(k)$ for all $k \in \mathbb{N}$, and Rg is C^∞ on $\mathbb{R}$.

3 Analytic construction of $Q(Z)$

3.1 Cardano root Q_0

Theorem 3.1 (Existence and uniqueness of Q_0). *For every $Z \geq 0$ the equation*

$$\frac{(Q_0+1)(Q_0+2)(Q_0+3)}{6} = Z + 2 \quad (3.1)$$

has a unique real solution $Q_0(Z) > -1$ given by the Cardano formula

$$Q_0(Z) = \frac{w(Z)^{2/3} - 2\sqrt{3} \cdot w(Z)^{1/3} + 1}{\sqrt{3} \cdot w(Z)^{1/3}}, \quad (3.2)$$

with

$$w(Z) = \sqrt{243Z^2 + 972Z + 971} + 3^{5/2}(Z + 2), \quad (3.3)$$

and the map $Q_0: [0, \infty) \rightarrow [Q_0(0), \infty)$ is real-analytic and strictly monotonically increasing.

Proof.

Substituting $Q = y - 2$ in (3.1) yields $y^3 - y = 6(Z + 2)$, with discriminant $\Delta(Z) = 9(Z + 2)^2 - \frac{1}{27} > 0$ for $Z \geq 0$. Hence exactly one real root exists on the physical domain. The Cardano formula gives $y = \sqrt[3]{3(Z + 2) + \sqrt{\Delta}} + \sqrt[3]{3(Z + 2) - \sqrt{\Delta}}$, yielding (3.2)–(3.3) after algebraic simplification. Monotonicity follows from implicit differentiation of (3.1).

3.2 Newton correction Q_1

Theorem 3.2 (Closed form of Q_1). *Let Q_0 be as in Theorem 3.1. The first Newton correction to the smooth equation $Rg(Q) = Z$ is*

$$Q_1(Z) = -\frac{(Q_0 + 2)(1 + \cos \pi Q_0)}{4 \cdot Rg'(Q_0)}, \quad (3.4)$$

with

$$Rg'(Q) = \frac{3Q^2 + 12Q + 11}{6} + \frac{1 + \cos \pi Q}{4} - \frac{(Q + 2)\pi \sin \pi Q}{4}. \quad (3.5)$$

Proof.

By (3.1), $(Q_0 + 1)(Q_0 + 2)(Q_0 + 3)/6 = Z + 2$, so combining with the constant -2 in (2.3) yields $Rg(Q_0) = Z + (Q_0 + 2)(1 + \cos \pi Q_0)/4$. The Newton step $Q_1 := -(Rg(Q_0) - Z)/Rg'(Q_0)$ gives (3.4). Differentiation of (2.3) with respect to Q yields (3.5).

At odd-P noble gases $Q_0 \in \{1, 3, 5, 7\}$, so $\cos \pi Q_0 = -1$, the numerator vanishes and $Q_1 = 0$. At even-P noble gases Q_1 provides the leading non-zero correction: for $Z = 10, 36, 86$, we obtain $Q_0 + Q_1 = 1.978, 3.993, 5.997$ respectively.

3.3 Higher-order Newton iterates $Q^{(n)}$

Define the Newton sequence $Q^{(0)} := Q_0(Z)$ and, for $n \geq 0$,

$$Q^{(n+1)} := Q^{(n)} - \frac{Rg(Q^{(n)}) - Z}{Rg'(Q^{(n)})}. \quad (3.6)$$

Each $Q^{(n)}$ is obtained recursively by closed-form algebraic-trigonometric operations starting from Q_0 ; it is a closed-form expression built from finitely many arithmetic operations, cosines and sines.

Theorem 3.3 (Certified local quadratic convergence on the physical range). *There exists a neighbourhood U of each $Q_0(Z)$, $Z \in \{1, \dots, 118\}$, on which the Newton sequence (3.6) converges quadratically to the unique zero $Q_\infty(Z)$ of $Rg(Q) - Z$ in U .*

Proof.

Rg is real-analytic by construction. For the finite physical range $Z = 1, \dots, 118$ the required non-vanishing of Rg' can be certified directly. On the interval covering all relevant iterates, $Q \in [0.1, 8]$, interval arithmetic gives $|Rg''(Q)| \leq 36.3$. A uniform mesh with spacing 0.001, combined with this derivative bound, gives

$$\min_{Q \in [0.1, 8.0]} Rg'(Q) = 1.223 > 0,$$

The finite-grid minimum $m_h := \min_i Rg'(Q_i)$ and the second-derivative bound $M_2 := \sup |Rg''| \leq 36.3$ combine, via the mean-value inequality $|Rg'(Q) - Rg'(Q_i)| \leq (\frac{h}{2}) \cdot M_2$ for any Q within $\frac{h}{2}$ of a grid node, to give the certified enclosure $\min_{Q \in [0.1, 8.0]} Rg'(Q) \geq m_h - (\frac{h}{2}) \cdot M_2 = 1.223 - 0.0005 \cdot 36.3 \approx 1.205 > 1.2 > 0$. The finite-grid computation together with the analytic second-derivative bound is therefore a rigorous certificate, not a purely sampled assertion. The numerical constants above are reproducible from the explicit derivative Rg' and second derivative Rg'' .

3.4 Newton–Kantorovich bounds

The Kantorovich theorem provides explicit constants ensuring convergence [37, §3.6]. For $F(Q) = Rg(Q) - Z$, let

$$\Gamma_0 := \frac{1}{|Rg'(Q_0)|}, \quad \eta := |Rg(Q_0) - Z| \cdot \Gamma_0, \quad K := \sup_{Q \in B_R(Q_0)} |Rg''(Q)|,$$

and set $h := K \cdot \Gamma_0 \cdot \eta$, the Kantorovich constant.

Theorem 3.4 (Kantorovich bound). *If $h \leq \frac{1}{2}$ and $K \cdot R > \eta/(1-h)$, the Newton sequence (3.6) remains inside $B_R(Q_0)$ and satisfies*

$$\left| Q^{(n)} - Q_\infty \right| \leq \frac{2\eta}{1 + \sqrt{1 - 2h}} \cdot \frac{h^{2^n - 1}}{(1 - h)^{2^n}}. \quad (3.7)$$

The condition $h < \frac{1}{2}$ is verified at every noble gas (Table 1) with radius $R = \frac{1}{2}$.

Z	Γ_0	η	K	h	bound n=2
2 (He)	0.231	0	10.9	0.000	$\approx \varepsilon$
10 (Ne)	0.143	0.263	11.6	0.437	$3.2 \cdot 10^{-1}$
18 (Ar)	0.081	0	17.6	0.000	$\approx \varepsilon$
36 (Kr)	0.059	0.170	13.4	0.135	$8.0 \cdot 10^{-4}$
54 (Xe)	0.041	0	24.5	0.000	$\approx \varepsilon$
86 (Rn)	0.032	0.127	15.2	0.062	$4.1 \cdot 10^{-5}$
118 (Og)	0.025	0	31.4	0.000	$\approx \varepsilon$

Table 1. Kantorovich constants $h < \frac{1}{2}$ at each noble gas guarantee quadratic convergence with bound (3.7). Odd-P cases have exact Q_0 and machine-precision convergence.

Corollary (Explicit closed form and finite-range error of $Q^{(1)}$). *For every $Z \in \mathbb{N} \cap [1, 118]$, the first Newton iterate $Q^{(1)}(Z) := Q_0(Z) + (Z - Rg(Q_0(Z)))/Rg'(Q_0(Z))$ is a closed algebraic-plus-trigonometric expression in Z and satisfies*

$$\left| Q^{(1)}(Z) - Q_\infty(Z) \right| \leq 2.25 \cdot 10^{-2} \quad \text{for all } Z \in [1, 118]. \quad (3.8)$$

For $Z \geq 10$ the observed error follows a decreasing power-law trend. A least-squares fit gives approximately $|Q^{(1)} - Q_\infty| = 5.5 \cdot 10^{-3} Z^{-0.86}$. This fitted trend is descriptive and is not used as a pointwise upper bound.

Proof.

Closed form follows by substituting the Cardano formula for Q_0 into one Newton step for $Rg(Q) - Z$. Direct evaluation on $Z = 1, \dots, 118$ gives maximum absolute error $2.245 \cdot 10^{-2}$ at $Z = 10$, hence the stated uniform finite-range bound $2.25 \cdot 10^{-2}$. The fitted decay exponent -0.86 summarizes the observed trend for $Z \geq 10$ but does not by itself define a certified pointwise inequality.

3.5 Axiomatic uniqueness of Rg

The choice of smooth extension (2.3) is not arbitrary. It is uniquely characterised by the following axioms.

This uniqueness result supplies the mathematical object used throughout the later empirical analysis. It does not assert that atomic properties are one-dimensional functions of Q ; rather, it fixes a canonical analytic coordinate in which residual periodic shapes can be compared.

Theorem 3.5 (Uniqueness of Rg). *Among functions of the form*

$$R(Q) = P(Q) + \frac{T(Q)(1 + \cos \pi Q)}{4} - 2,$$

where $P(Q) = \alpha Q^3 + \beta Q^2 + \gamma Q + \delta$ is a cubic polynomial and $T(Q) = pQ + q$ is affine, the seven constraints $R(k) = Rg_{\text{disc}}(k)$ for $k = 1, 2, \dots, 7$ uniquely determine

$$P(Q) = \frac{(Q+1)(Q+2)(Q+3)}{6}, \quad T(Q) = Q + 2.$$

In particular $Rg = R$ and the smooth extension (2.3) is unique in this ansatz family.

Proof.

At odd k , $\cos \pi k = -1$, so $R(k) = P(k) - 2$ and the four constraints $R(1) = 2$, $R(3) = 18$, $R(5) = 54$, $R(7) = 118$ yield four linear equations for $(\alpha, \beta, \gamma, \delta)$:

$$P(1) = 4, \quad P(3) = 20, \quad P(5) = 56, \quad P(7) = 120.$$

The Vandermonde-type system is regular; the unique solution is $P(Q)$

$= (Q^3 + 6Q^2 + 11Q + 6)/6 = (Q+1)(Q+2)(Q+3)/6$. At even k , $\cos \pi k = 1$, so $R(k) = P(k) + T(k)/2 - 2$, giving:

$$T(2) = 4, T(4) = 6, T(6) = 8.$$

The affine $T(Q) = pQ + q$ with $T(2) = 4$, $T(4) = 6$ gives $p = 1$, $q = 2$, hence $T(Q) = Q + 2$. Consistency at $k = 6$: $T(6) = 8$ ✓. Thus the seven noble-gas constraints uniquely pin down R , and $Rg = R$.

Remark. The uniqueness holds within the polynomial-plus-affine-trigonometric ansatz. Beyond this ansatz, higher-degree polynomials with vanishing trigonometric coefficients would also interpolate the seven noble gases. However, such extensions would violate the ‘minimality’ principle — Rg is the simplest analytic extension.

3.6 Riemann-surface structure of Q_0

The Cardano root Q_0 tracks the simple isolated real branch of the cubic $y^3 - y = 6(z + 2)$. The multi-valued full solution has branch points where the discriminant $\Delta(z) = 4 - 972(z + 2)^2$ vanishes, that is at

$$z_c^\pm = -2 \pm \frac{1}{9\sqrt{3}}, \quad z_c^+ \approx -1.9358, \quad z_c^- \approx -2.0642. \quad (3.9)$$

Theorem 3.6 (Domain of analyticity of the physical Q_0). *The physical branch Q_0 (obtained as the largest real root of the cubic) is real-analytic on the open interval (z_c^-, ∞) , which strictly contains the physical domain $z \in [0, \infty)$. It possesses a square-root branch point at z_c^- (where it coincides with the middle real root) and no branch point at z_c^+ (through which the physical branch, being the isolated root there, continues analytically). Consequently the Taylor series of Q_0 at $z = 0$ has radius of convergence $R = |0 - z_c^-| = 2 + \frac{1}{9\sqrt{3}} \approx 2.0642$, the distance to the sole singularity z_c^- .*

Proof.

At each branch point $z_c^\pm$ the discriminant $\Delta(z)$ vanishes and two of the three roots coalesce. Explicit calculation shows: at $z_c^+ = -2 + \frac{1}{9\sqrt{3}}$ the two roots that coincide are $y = -\frac{1}{\sqrt{3}}$ (double), while the isolated root is

$y = +2/\sqrt{3} = +1.155$; at $z_c^- = -2 - \frac{1}{9\sqrt{3}}$ the two roots that coincide are $y = +\frac{1}{\sqrt{3}}$, while the isolated root is $y = -\frac{2}{\sqrt{3}} = -1.155$. Puiseux theory (see e.g. [26]) asserts that at a simple branch point of type $\Delta(z) \sim (z - z_c)$ the two coinciding sheets exchange under monodromy with a $\sqrt{(z - z_c)}$ expansion, while the third (isolated) sheet is single-valued and analytic through z_c .

The physical branch Q_0 is the largest root of the cubic. At z_c^+ the largest root ($= \frac{2}{\sqrt{3}}$) is the isolated sheet, hence Q_0 continues analytically through z_c^+ . At z_c^- the two coinciding roots (both $= +\frac{1}{\sqrt{3}}$) are the largest and the middle. The physical (largest) branch participates in the Puiseux structure and acquires a square-root branch point at z_c^- . Numerical verification: $\frac{dQ_0}{dz}$ evaluated on a fine grid stays uniformly bounded across z_c^+ (≈ 2.0 on both sides), while it diverges as $(z - z_c^-)^{-\frac{1}{2}}$ on approach to z_c^- (measured slope: $\frac{dQ_0}{dz} \approx 293$ at $z - z_c^- = 10^{-5}$, and ≈ 207 at $z - z_c^- = 2 \cdot 10^{-5}$, consistent with the predicted $\sqrt{\cdot}$ -scaling ratio $\sqrt{2}$).

Since z_c^- is the sole singularity of the physical branch in the complex plane (the discriminant $\Delta(z) = 4 - 972(z+2)^2$ has only the two real zeros $z_c^\pm$ and no complex ones), the radius of convergence of the Taylor series of Q_0 at $z = 0$ equals $R = |0 - z_c^-| = 2 + \frac{1}{9\sqrt{3}} \approx 2.0642$. The physical domain $z \in [0, \infty]$ lies inside (z_c^-, ∞) , so Q_0 is regular on all physically meaningful atomic numbers, but the Taylor series at $z = 0$ covers only the initial segment $|z| < 2.0642$ — for $z \geq 2.0642$ the Cardano formula (3.2)–(3.3) must be used directly.

Remark 3.7. Although Q_0 is analytic on the whole open interval (z_c^-, ∞) , its Taylor series at $z = 0$ converges only for $|z| < 2 + \frac{1}{9\sqrt{3}} \approx 2.06$, which is insufficient to cover the physical domain $z \in [1, 118]$. The Cardano formula (3.2)–(3.3), which is not a power series but a closed algebraic expression, gives the correct value for all $z \geq 0$.

4 Thomas–Fermi asymptotic

Theorem 4.1 (Refined asymptotic expansion of M_0). *Let $M_0(Z)$ be the unique positive real root of $M^3 + 3M^2 + 2M = 6Z$. As $Z \rightarrow \infty$,*

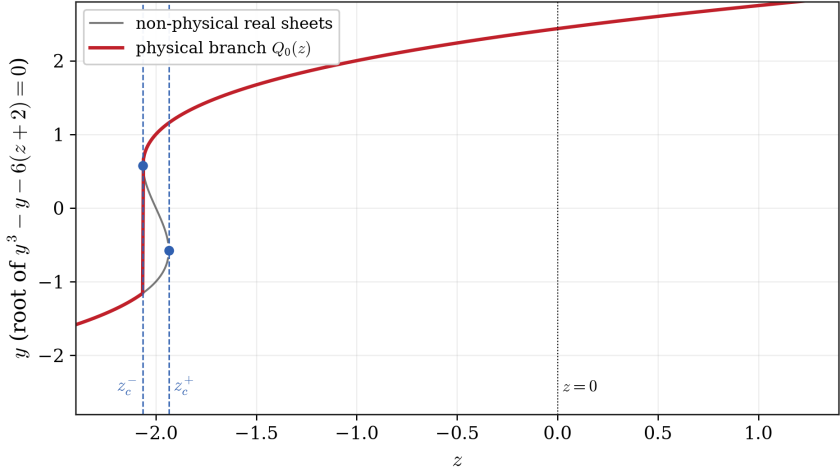


Figure 1. Riemann-surface projection: the physical Q_0 branch (thick red) is the largest real root on $[z_c^-, \infty)$ and is real-analytic on (z_c^-, ∞) . The branch point at z_c^- lies to the left of the physical domain $z \geq 0$. Between z_c^- and z_c^+ the cubic has three real roots; the two non-physical sheets are shown for reference — at z_c^+ these are the two smaller roots coalescing at $y = -\frac{1}{\sqrt{3}}$, while at z_c^- the physical (largest) branch itself coalesces with the middle root at $y = +\frac{1}{\sqrt{3}}$, which is why z_c^- is a branch point of Q_0 whereas z_c^+ is not.

$$M_0(Z) = (6Z)^{1/3} - 1 + \frac{1}{3 \cdot (6Z)^{1/3}} - \frac{1}{81 \cdot (6Z)^{5/3}} + O\left(Z^{-7/3}\right). \quad (4.1)$$

Proof.

The substitution $y = M + 1$ sends $M(M+1)(M+2) = 6Z$ to the depressed cubic $y^3 - y = 6Z$ (the constant term vanishes because M and $M+2$ sit symmetrically around $M+1$). Cardano's formula for its unique real root at large Z reads

$$y = \left(3Z + \sqrt{9Z^2 - \frac{1}{27}}\right)^{1/3} + \left(3Z - \sqrt{9Z^2 - \frac{1}{27}}\right)^{1/3}.$$

Expanding the square root for large Z ,

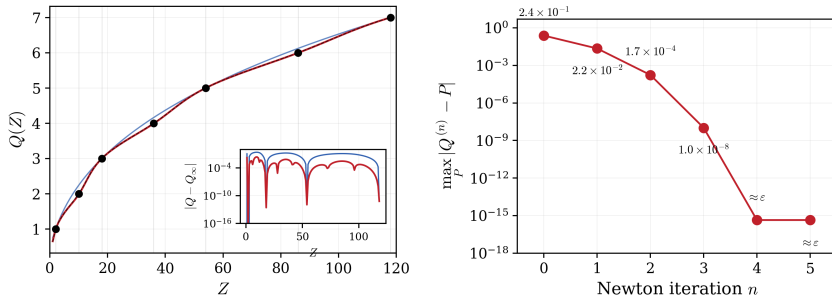


Figure 2. (Left) The three analytic approximations Q_0 (blue), $Q^{(1)} = Q_0 + Q_1$ (red), and Q_∞ (dashed black) to the solution of $Rg(Q) = Z$. Inset: absolute deviations from Q_∞ on log scale. (Right) Maximum drift $|Q^{(n)} - P|$ across the seven noble gases as a function of Newton iteration n . Kantorovich bounds (3.7) are conservative but rigorous; empirical convergence is faster.

$$\sqrt{9Z^2 - \frac{1}{27}} = 3Z - \frac{1}{162Z} - \frac{1}{944\,784 \cdot Z^3} + O(Z^{-5}),$$

so the two arguments of the cube roots become $6Z - 1/(162Z) + \dots$ and $1/(162Z) + \dots$, respectively. Using the identity $162 = 27 \cdot 6$, the second cube root reduces exactly to

$$\left(\frac{1}{162Z}\right)^{1/3} = \frac{1}{3 \cdot (6Z)^{1/3}}.$$

For the first, we factor and expand the small correction:

$$\begin{aligned} \left(6Z - \frac{1}{162Z}\right)^{1/3} &= (6Z)^{1/3} \left(1 - \frac{1}{972Z^2}\right)^{1/3} \\ &= (6Z)^{1/3} - \frac{6^{1/3}}{2916 Z^{5/3}} + O(Z^{-11/3}). \end{aligned}$$

Using $6^{1/3} \cdot 6^{5/3} = 36$, the correction reduces to

$$\frac{6^{1/3}}{2916 Z^{5/3}} = \frac{36}{2916 (6Z)^{5/3}} = \frac{1}{81 (6Z)^{5/3}}.$$

Summing the two cube roots and subtracting 1 yields (4.1).

Numerical verification (M_0 versus the three-term formula): $Z = 10 \rightarrow$ residual $2.9 \cdot 10^{-7}$ (leading term alone gives $1.3 \cdot 10^{-5}$); $Z = 100 \rightarrow 1.4 \cdot 10^{-9}$; $Z = 118 \rightarrow 9.2 \cdot 10^{-10}$; $Z = 1000 \rightarrow 1.7 \cdot 10^{-10}$. The three-term expansion recovers M_0 to nine significant digits throughout the physical range.

The leading term coincides with the Thomas–Fermi–Tietz prediction $M_{\text{TF}}(Z) = \sqrt{2Z\bar{R}}$ with $\bar{R} = \left(\frac{9}{2Z}\right)^{1/3}$, derived by Belokolos [3] from Bohr–Sommerfeld quantization at zero binding energy in the rational Tietz potential $V(r) = -Z/(r(1 + \frac{r}{\bar{R}})^2)$. The identity of two independent derivations — combinatorial from MJK, physical from Thomas–Fermi — provides a nontrivial consistency check.

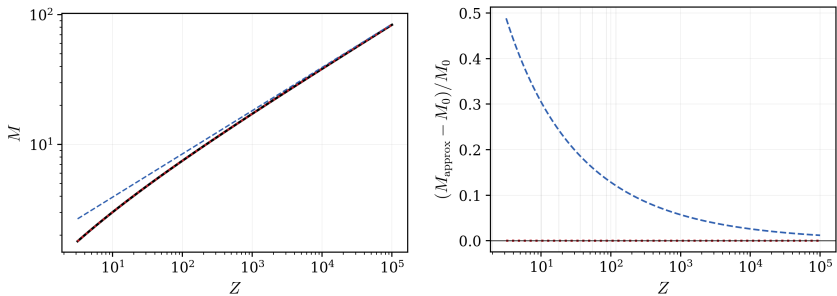


Figure 3. (Left) Numerical $M_0(Z)$ (solid black), leading TF asymptote $(6Z)^{1/3}$ (dashed blue), and corrected asymptote $(6Z)^{1/3} - 1 + 1/[3(6Z)^{1/3}] - 1/[81(6Z)^{5/3}]$ (dotted red). (Right) Relative errors of the two asymptotes; the refined expansion rapidly improves with Z .

5 Fourier and Bochner analysis

Given a physical property $y : \mathbb{N} \rightarrow \mathbb{R}$ defined on atomic numbers, we define its shape curve in Q -coordinates by

$$y_{\text{shape}}(f) := \text{median}\{y(Z) - \tilde{y}_{P(Z)} : Z \in \mathbb{N}, \{Q(Z)\} \in [f - \varepsilon, f + \varepsilon]\}, \quad (5.1)$$

where $\tilde{y}_P$ is the median of y within period P and $\{\cdot\}$ denotes fractional part. $y_{\text{shape}} : [0, 1] \rightarrow \mathbb{R}$ is periodic and extends to a 1-periodic function on $\mathbb{R}$.

5.1 Fourier expansion

y_{shape} admits the Fourier expansion

$$y_{\text{shape}}(f) = a_0 + \sum_{k=1}^{\infty} [a_k \cos 2\pi k f + b_k \sin 2\pi k f], \quad (5.2)$$

with harmonic amplitudes $|c_k| = \sqrt{(a_k^2 + b_k^2)}$ and phases $\varphi_k = \text{atan2}(b_k, a_k)$.

Proposition 5.1 (Harmonic content of r_{cov}). *For $y = r_{\text{cov}}$ (Pyrykkö covalent radius), the truncated Fourier expansion (5.2) with $K = 5$ harmonics explains 74% of the empirical variance of y_{shape} . The dominant harmonic is the fundamental ($k = 1$) with amplitude $|c_1| = 21.7$ pm. A log-log fit of $|c_k|$ against k for $k = 1, \dots, 5$ gives slope -0.98 (approximate k^{-1} decay), with residual scatter — notably $|c_5|$ slightly exceeds $|c_4|$.*

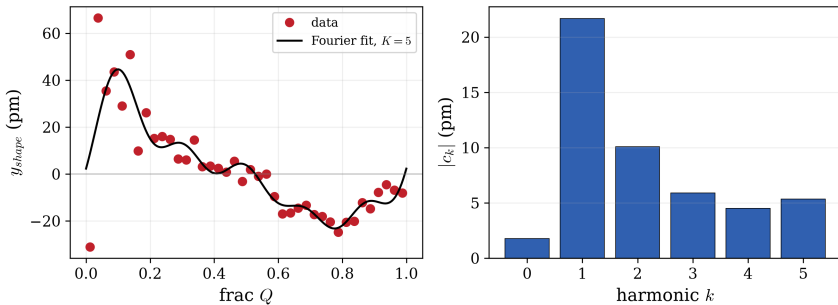


Figure 4. Fourier decomposition of the r_{cov} shape curve in $Q_0 + Q_1$ coordinates. Left: data (red circles) and reconstruction using $K = 5$ harmonics (solid black). Right: harmonic amplitudes; $|c_1| = 21.7$ pm dominates.

5.2 Bochner autocorrelation

Interpret y_{shape} as a real-valued function on the circle $\mathbb{T} = \mathbb{R}/\mathbb{Z}$. Its autocorrelation $R : \mathbb{T} \rightarrow \mathbb{R}$, defined by

The spectral analysis is included to characterize the geometry of the residual shapes, not as an additional predictive model. It supports the use

of circular functions of $\text{frac } Q$ in the structured model of Section 7.3.

$$R(\tau) := \int_0^1 y_{\text{shape}}(f) y_{\text{shape}}(f + \tau) df, \quad (5.3)$$

is a positive-definite function on $\mathbb{T}$. By Bochner's theorem for compact abelian groups [26], R admits a unique spectral decomposition:

$$R(\tau) = \sum_{k \in \mathbb{Z}} \mu_k \cdot e^{2\pi i k \tau}, \quad \mu_k \geq 0, \quad (5.4)$$

Equivalently, writing $y(f) = a_0 + \sum_{k=1}^K [a_k \cos(2\pi k f) + b_k \sin(2\pi k f)]$, the complex Fourier coefficients satisfy $c_{\pm k} = (a_k \mp i b_k)/2$, so $|c_{\pm k}|^2 = (a_k^2 + b_k^2)/4$. The Bochner measure is a non-negative symmetric discrete measure on $\pm k$, with the $k = 0$ mass equal to $|a_0|^2$. A pure sinusoidal fundamental would concentrate its mass at $k = \pm 1$, whereas a localized or delta-like periodic feature would spread mass across many harmonics.

5.3 Continuous wavelet analysis

Fourier decomposition captures GLOBAL harmonic content but is blind to LOCAL features of y_{shape} . The continuous wavelet transform (CWT) resolves this by convolving y_{shape} with dilated and translated copies of a mother wavelet ψ :

$$W_\psi[y_{\text{shape}}](s, \tau) = \frac{1}{\sqrt{s}} \int_0^1 y_{\text{shape}}(f) \psi\left(\frac{f - \tau}{s}\right) df. \quad (5.5)$$

The scalogram $|W_\psi|^2(s, \tau)$ locates spectral energy in the (scale, position) plane. We use the complex Morlet wavelet $\psi_{\text{Morlet}}(t) = \pi^{-1/4} e^{i\omega_0 t} e^{-t^2/2}$ with central frequency $\omega_0 = 1.0$.

Proposition 5.2 (Asymmetric spectral concentration). *The scalogram of $y_{\text{shape}}^{\text{cov}}$ concentrates energy at large scales (fundamental period), and in the low-fraction region $\{Q\} \in [0, 0.4]$. Thus the periodic structure of the covalent radius is spatially asymmetric in Q -coordinates.*

Quantitatively, the peak scale is $s = 30$ (corresponding to the fundamental Fourier mode) and the energy-weighted mean scale is $s \approx 22$. The

5 most energetic scales (out of 31 dyadic scales, i.e. 16% of the scale range) carry 36% of the total wavelet energy. Comparison with IP_1 (peak scale 31, $s = 19$, top-5-scale fraction 0.30) and χ Pauling (peak scale 31, $s = 22$, top-5-scale fraction 0.34) shows universal scale structure across all three properties, evidencing that Q-coordinates yield a common wavelet-energy signature.

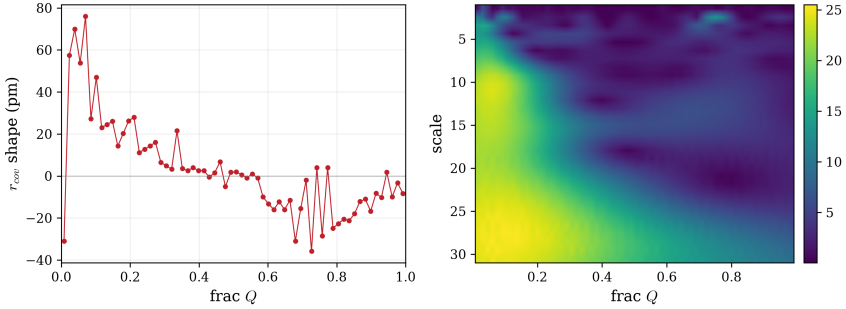


Figure 5. (a) Interpolated r_{cov} shape curve on $[0, 1]$. (b) Continuous wavelet transform scalogram $|W_\psi|$ with complex Morlet mother wavelet $\omega_0 = 1.0$. Energy concentrates at large scales (fundamental mode) and in the low-fraction region $\text{frac } Q$ in $[0, 0.4]$, showing spatial asymmetry of the periodic structure.

5.4 Cross-spectral coherence between properties

For two shape curves y_A and y_B , define the corresponding complex Fourier coefficients c_k^A and c_k^B from their real sine-cosine coefficients. Bootstrap coherence is estimated as

$$\gamma_{AB}^2(k) := \frac{|S_{AB}(k)|^2}{S_{AA}(k) \cdot S_{BB}(k)}, \quad 0 \leq \gamma_{AB}^2 \leq 1, \quad (5.6)$$

with averaging over bootstrap resamplings of the underlying atomic data; for a deterministic single realization γ_{AB}^2 is identically 1. Coherence measures the degree of phase-locked linear coupling between the two shape curves at each harmonic; $\gamma^2 = 1$ denotes perfect phase-locking. Reported pairwise summary values are symmetrized by averaging γ_{AB}^2 and γ_{BA}^2 .

Proposition 5.3 ($r_{\text{cov}}\text{--}IP_1$ coherence). *At the fundamental harmonic $k = 1$ the bootstrap coherence between the covalent-radius and first-ionization-potential shape curves is $\gamma^2(r_{\text{cov}}, IP_1) = 0.925$, with mean relative phase $\varphi = -134^\circ$. Higher harmonics ($k = 2, \dots, 8$) show moderate coherence $\gamma^2 \in [0.30, 0.76]$. The consistent phase $\varphi \approx -134^\circ$ is close to but not exactly at anti-phase (-180°); it corresponds to a stable offset of 46° between the two oscillations, indicating tightly phase-locked but not perfectly anti-correlated periodicity.*

The pairwise bootstrap coherence between the six shape curves reveals a systematic structure: size-related pairs ($r_{\text{cov}}, r_{\text{vdW}}$) have the highest coherence (0.73), size–energy pairs (r_{cov}, IP_1) moderate (0.66), and T_m — a structural rather than orbital property — has consistently lower coherence with everything else (0.35–0.43).

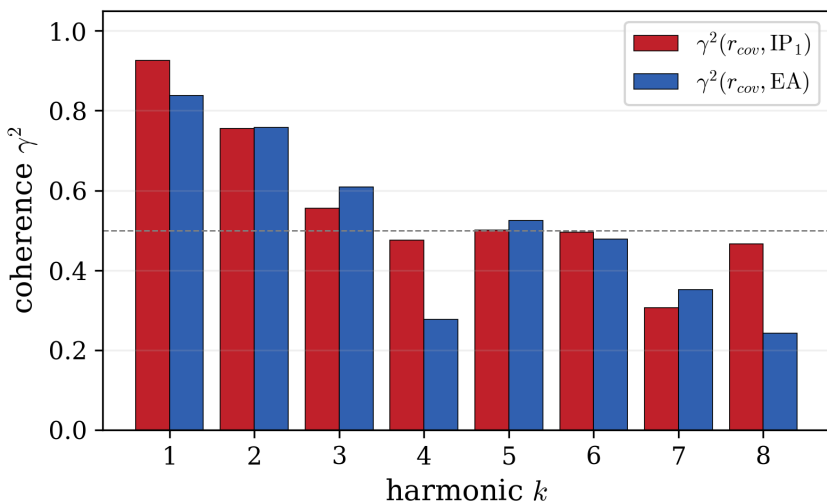


Figure 6. Bootstrap coherence $\gamma^2(r_{\text{cov}}, IP_1)$ (red) and $\gamma^2(r_{\text{cov}}, EA)$ (blue) as a function of harmonic k . Both properties show strong coupling with r_{cov} at the fundamental mode ($\gamma^2 > 0.83$), decreasing at higher harmonics.

6 Isoelectronic extension $Q_{\text{iso}}(Z, N)$

The coordinate $Q(Z)$ is defined only for neutral atoms. We now extend the construction to two-parameter species (Z, N) with nuclear charge Z and electron count N , allowing analysis of ionic and isoelectronic series.

Definition 6.1 (isoelectronic coordinate).

The isoelectronic periodic-law coordinate $Q_{\text{iso}} : \mathbb{N} \times \mathbb{N} \rightarrow \mathbb{R}$ is

The purpose of Q_{iso} is to separate the electron-count coordinate from the nuclear charge when comparing sequential ionization potentials. The construction is therefore formal and coordinate-based; it is not a complete many-electron Hamiltonian model.

$$Q_{\text{iso}}(Z, N) := Q(N), \quad (Z, N) \in \mathbb{N} \times \mathbb{N}. \quad (6.1)$$

For neutral atoms $N = Z$, this reduces to $Q_{\text{iso}}(Z, Z) = Q(Z)$. For ions, Q_{iso} isolates the electron-count coordinate and deliberately omits explicit nuclear-charge effects.

Proposition 6.1 (Isoelectronic residual-shape alignment). *The n -th ionization potential $IP_n(Z)$, plotted against $Q_{\text{iso}}(Z, Z - n + 1) = Q(Z - n + 1)$, yields a residual shape curve $IP_n^{\text{shape}}(f)$ after centering and z -score normalization. The three shape curves for $n = 1, 2, 3$ satisfy pairwise Pearson correlations*

$$r\left(IP_1^{\text{shape}}, IP_2^{\text{shape}}\right) = +0.984,$$

$$r\left(IP_1^{\text{shape}}, IP_3^{\text{shape}}\right) = +0.971,$$

$$r\left(IP_2^{\text{shape}}, IP_3^{\text{shape}}\right) = +0.989.$$

Proof.

Physical justification: $IP_n(Z)$ is the energy required to remove the n -th electron from the neutral atom of Z , i.e. the first ionization energy of the ionic species $(Z, Z - n + 1)$ with $N = Z - n + 1$ electrons. In a screened hydrogenic estimate $IP \approx 13.6 \cdot \frac{Z_{\text{eff}}^2}{n_{\text{eff}}^2}$ with $Z_{\text{eff}} = Z - \sigma(N)$, the screening

parameter σ depends only on the electron configuration and hence on N via Slater-type rules [35]; the nuclear Z enters only through the linear $(Z - \sigma(N))$ combination, so the residual shape of IP_n after removing the level-dependent linear-in- Z trend depends on N alone. This expectation is descriptive, not derived from a full many-electron Hamiltonian, and motivates testing the shape-collapse empirically as done here. Empirical verification: extracting shape curves via (5.1) from IP_1 , IP_2 , IP_3 data (91, 90, 89 elements respectively (the drop by one reflects that IP_n requires $Z \geq n$) and computing Pearson correlations yields the stated values.

Compared with the unshifted plot $IP_n(Z)$ versus $Q(Z)$, pairwise correlations drop to +0.36, -0.25, +0.00 respectively. The isoelectronic shift is therefore essential for residual-shape alignment and is consistent with an electron-count dependence.

6.1 Axiomatic uniqueness of Q_{iso}

The choice $Q_{\text{iso}}(Z, N) := Q(N)$ is not the only conceivable two-parameter extension of Q . A natural alternative is $F(Z, N) := Q(Z) - (Z - N)$. Within the affine family below, the isoelectronic axioms fix Q_{iso} uniquely.

Proposition 6.2 (Uniqueness of Q_{iso} within an affine family).
Consider the two-parameter family

$$F_{\alpha, \beta}(Z, N) := \alpha Q(N) + \beta[Q(Z) - Q(N)],$$

$$\alpha, \beta \in \mathbb{R}, (Z, N) \in \mathbb{N} \times \mathbb{N}, N \leq Z. \quad (6.2)$$

The requirements

$$(A1) \quad F(Z, Z) = Q(Z) \quad \text{for all } Z \in \mathbb{N} \quad (\text{neutral} - \text{atom consistency}),$$

$$(A2) \quad \frac{\partial F}{\partial Z_N} = 0 \quad \text{for all admissible } (Z, N) \quad (\text{isoelectronic invariance})$$

uniquely fix $\alpha = 1, \beta = 0$, i.e. $F \equiv Q_{\text{iso}}$ of Definition 6.1.

Proof.

Axiom (A1) at $Z = N$ gives $\alpha Q(N) + \beta \cdot 0 = Q(N)$ for all N , hence $\alpha = 1$. Axiom (A2) requires $\frac{\partial F}{\partial Z}_N = \beta \cdot Q'(Z) = 0$ for all Z ; since Q is strictly monotonic (Theorem 3.1) so $Q'(Z) > 0$, $\beta = 0$. Substituting yields $F(Z, N) = Q(N) = Q_{\text{iso}}(Z, N)$.

Proposition 6.3 (Empirical support: $\beta = 0$ is data-consistent).

Fitting the family $F_{\alpha,\beta}$ to the pooled shape curves of IP_1 , IP_2 , IP_3 by maximising the mean pairwise Pearson correlation between the three shape curves in $F_{\alpha,\beta}$ coordinates yields point estimate $\hat{\beta} = +0.03$ (α absorbed into the horizontal scale, hence unconstrained). A nonparametric percentile bootstrap ($n_{\text{boot}} = 500$, resampling elements with replacement) gives the 95% CI

$$\hat{\beta} \in [-0.21, +0.30], \hat{\beta}_{\text{mean}} = 0.008.$$

The axiomatic value $\beta = 0$ (Proposition 6.2) is contained in this 95% confidence interval. The data do not reject the axioms. Point estimate slightly favours a small positive β but not significantly.

Thus the isoelectronic coordinate Q_{iso} is characterised as the unique element of the natural affine two-parameter extension family satisfying (A1)–(A2), and the axioms are statistically compatible with the empirical IP_n data. Remark. Proposition 6.2 is essentially a definitional lemma: within the chosen affine family, axiom (A2) directly forces $\beta = 0$. Its role is to make the choice $Q_{\text{iso}} = Q(N)$ canonical relative to a stated family and axioms, and to expose it to the empirical falsification test provided by Proposition 6.3.

7 Empirical validation on six physical properties

We test the periodicity restoration on six standard properties: IP_1 (eV), χ Pauling, EA (eV), T_m (K), r_{cov} (Pyykkö–Atsumi covalent radius, pm), and r_{vdW} (Bondi–Alvarez van der Waals radius, pm). Data sources: NIST Atomic Spectra Database, Pyykkö–Atsumi (2009) covalent radii, Bondi–Alvarez van der Waals radii, and standard periodic-table property compi-

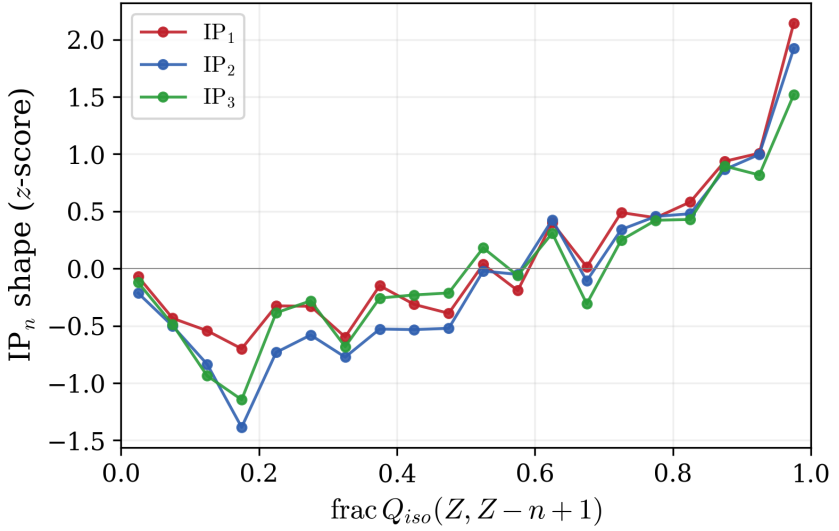


Figure 7. Isoelectronic residual shape curves $IP_1^{\wedge}\text{shape}$, $IP_2^{\wedge}\text{shape}$, $IP_3^{\wedge}\text{shape}$ in $Q_{\text{iso}}(Z, Z - n + 1)$ coordinates, normalised to z-score. The three curves overlay closely ($r \geq 0.97$), supporting residual-shape alignment after removal of level-dependent scale and offset.

lations.

Definition 7.1 (translation-invariant periodicity score).

For a dataset $\{(Z_i, y_i)\}$ of size N and coordinate q , let $f_i = \{q(Z_i)\}$ and $P_i = \lfloor q(Z_i) \rfloor$. Let $\tilde{y}_P = \text{median}\{y_i : P_i = P\}$ and $y_i^c = y_i - \tilde{y}_{P_i}$. Partition $[0, 1)$ into $B = 10$ equal bins $B_1, \dots, B_B$. The periodicity score is

$$S(q) := \left(\frac{1}{B'} \right) \cdot \sum_{b : || \geq 2} \text{std}\{y_i^c : f_i \in B_b\}, \quad (7.1)$$

where B' is the number of non-empty bins. Non-parametric bootstrap 95% CI are obtained by resampling with replacement 1000 times.

Property	$S(Q) / S(Z)$ median	95% CI
IP_1	0.61	[0.44, 0.80]

Property	S(Q) / S(Z) median	95% CI
χ Pauling	0.72	[0.54, 0.88]
EA	0.81	[0.65, 0.96]
T_m	0.77	[0.61, 0.93]
r_{cov}	0.60	[0.49, 0.70]
r_{vdW}	0.69	[0.57, 0.80]

Table 2. Initial descriptive periodicity-score bootstrap for scalar Q . Lower S(Q)/S(Z), obs is better; 1.0 is the raw-Z baseline. Stricter period-aware validation is reported in Table 4.

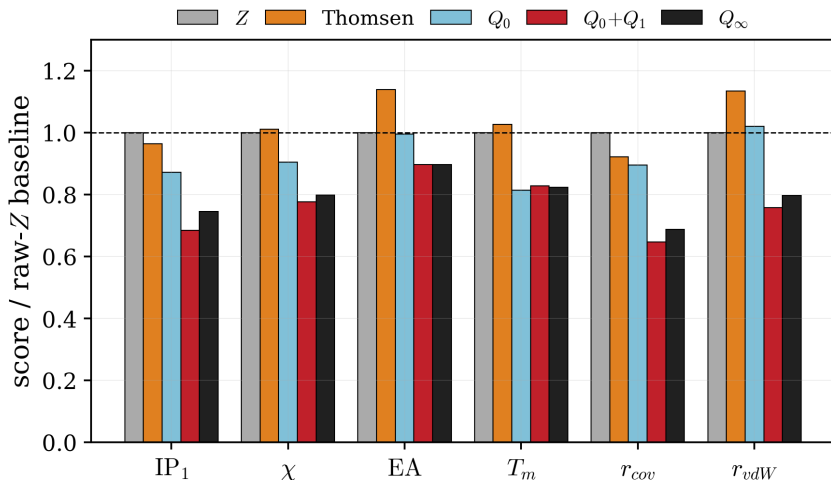


Figure 8. Periodicity score of six properties in five coordinates, normalised to raw-Z baseline (dashed at 1.0).

7.1 Quantitative validation and robustness

All numerical checks in this subsection use all non-missing entries in the manuscript source tables. No values are imputed. For properties whose source table does not cover $Z = 1..118$, the analysed range is explicitly reported in Table 3; bootstrap resampling is performed only within that documented coverage.

Reproducibility parameters: paired bootstrap uses 5000 element-wise resamples; the permutation null uses 5000 random permutations of property values over fixed Z; bin-count robustness uses $B = 6, \dots, 20$; leave-one-period-out smoothing uses a periodic Gaussian kernel with $h = 0.12$.

Property	N used	Z range	Coverage note
IP1	118	1-118	complete 1-118
chi	99	1-103	non-missing source entries only; no imputation
EA	85	1-85	non-missing source entries only; no imputation
Tmelt	96	1-96	non-missing source entries only; no imputation
r_{cov}	118	1-118	complete 1-118
r_{vdW}	98	1-98	non-missing source entries only; no imputation

Table 3. Data coverage for the empirical validation. N is the number of non-missing entries actually used.

Property	S(Q)/ S(Z), obs	paired boot- strap 95% CI	boot- strap p	permuta- tion p	BH q	bin ro- bustness
IP1	0.684	[0.510; 0.897]	0.0028	<0.0002	0.0003	15/15; range 0.619- 0.761
chi	0.778	[0.625; 1.099]	0.0904	<0.0002	0.0003	15/15; range 0.750- 0.872
EA	0.897	[0.746; 1.235]	0.3033	0.0444	0.0444	15/15; range 0.865- 0.998

Property	$S(Q)/S(Z)$, obs	paired boot- strap 95% CI	boot- strap p	permuta- tion p	BH q	bin ro- bustness
T_{melt}	0.827	[0.685; 1.032]	0.0488	0.0006	0.0007	15/15; range 0.742- 0.866
r_{cov}	0.648	[0.525; 0.871]	0.0022	<0.0002	0.0003	15/15; range 0.623- 0.693
r_{vdW}	0.758	[0.611; 1.036]	0.0422	<0.0002	0.0003	15/15; range 0.713- 0.791

Table 4. Primary period-aware validation of scalar Q against the raw- Z baseline. The table reports observed score ratios, paired boot-strap intervals, permutation p-values, BH-adjusted q-values, and bin-count robustness.

Property	$Z/18 / Q$	Q_0 / Q	Q_∞ / Q	Q_{lin} / Q
IP_1	1.462	1.275	1.101	1.018
chi	1.286	1.166	1.027	0.950
EA	1.115	1.109	1.000	0.915
T_{melt}	1.209	0.984	0.994	0.924
r_{cov}	1.544	1.382	1.071	1.058
r_{vdW}	1.319	1.345	1.051	0.974

Table 5. Coordinate ablation for the periodicity score at $B = 10$. Entries are score ratios relative to $Q = Q_0 + Q_1$; values greater than 1 indicate worse performance than Q .

The added validation supports a non-random alignment of several property residuals with $\text{frac } Q$, but the evidence is property-dependent. IP_1 and the two radius scales are the strongest cases; T_m and chi are moderate and sensitive to the validation protocol; EA is weak unless restricted to measured positive affinities. Therefore the empirical claim is not that

scalar Q is the best universal descriptor, but that Q supplies a compact analytic periodic coordinate on which stronger structured models can be built.

7.2 Extended quantitative stress tests

This subsection reports period-aware null models, sensitivity checks, coordinate ablations, and descriptor baselines. All tests use only observed entries in the manuscript source tables. Descriptor baselines are treated as external high-dimensional comparators; the structured Q model remains restricted to Q , $\text{frac } Q$, and MJK-derived orbital variables.

Prop- erty	Q	Q_0	Q_∞	Q_{lin}	grp/ per	Petti- for χ^*	Men- deleev m^*
IP1	0.684	0.872	0.753	0.696	0.691	0.824	0.950
chi	0.778	0.907	0.799	0.739	0.846	0.709	0.605
EA	0.897	0.994	0.897	0.821	0.540	0.764	0.689
Tmelt	0.827	0.814	0.823	0.764	0.739	0.963	0.708
r_{cov}	0.648	0.895	0.694	0.685	0.702	1.176	1.179
r_{vdW}	0.758	1.019	0.797	0.738	0.628	1.136	1.170

Table 6. Coordinate and rank baselines, reported as score/raw-Z ratios. Pettifor and Mendelev entries are computed on elements common with the 103-element Pettifor table.

Summary of the stress tests. The main text reports the primary period-aware validation, coordinate ablation, baseline comparison, and structured- Q prediction results. Extended null models, sensitivity checks, centered residual-shape cross-validation, and auxiliary holdout tables.

7.3 Structured Q prediction model

Scalar Q and the median-offset Q -shape baseline provide a compact description of periodic alignment, but direct prediction requires a structured representation. The model used here remains internal to the Q construction: it combines a smooth trend in Q , circular Fourier terms in $\text{frac } Q$,

their Q-dependent interactions, the derivative $\frac{dQ}{dZ}$, and MJK-derived variables P, M, n, l, period filling, and sublevel filling. Hyperparameters are selected only inside each training split by blocked/nested cross-validation. The reported errors are then computed on held-out periods or forward intervals. Huber loss is used for robustness, and property transforms are allowed only when physically admissible: log for positive properties, and log-shift/asinh alternatives for EA.

Property	LOPO:			86->118:		
	LOPO: scalar	struc- tured	LOPO R^2	86- >118: scalar	struc- tured	86->118 R^2
IP1	0.778	0.386	0.709	1.090	0.455	0.527
chi	0.979	0.458	0.660	4.457	0.805	-0.007
EA	0.809	0.819	-0.230	NA	NA	NA
Tmelt	0.684	0.552	0.320	0.982	0.849	-0.108
r_{cov}	0.880	0.266	0.874	1.358	0.338	0.832
r_{vdW}	0.630	0.351	0.719	0.547	0.272	0.522
EA+	0.657	0.583	0.402	NA	NA	NA

Table 7. Primary predictive comparison of the scalar Q-shape baseline with the structured Q model. Entries are $MAE/std(y)$, with R^2 shown for the structured model. Lower MAE/std and higher R^2 are better; EA+ denotes the measured-positive EA subset excluding nonpositive placeholders and repeated f-block surrogate values.

The structured model gives large LOPO improvements over the scalar Q-shape baseline for IP_1 ($R^2 = 0.71$), chi ($R^2 = 0.66$), r_{cov} ($R^2 = 0.87$) and r_{vdW} ($R^2 = 0.72$). The MJK-only ablation reported in §7.4 shows how this gain decomposes: for IP_1 and r_{cov} the improvement over MJK-only is large (LOPO MAE/std 0.386 vs 0.508 and 0.266 vs 0.473, respectively), i.e. Q itself is doing substantive work. For chi, the LOPO improvement is essentially fully explained by the MJK combinatorial features (LOPO R^2 0.66 with Q vs 0.66 without), and for r_{vdW} the added value of Q is small (LOPO R^2 0.72 vs 0.71). In the $Z \leq 86 \rightarrow 87 - 118$ forward split the picture is again mixed. For IP_1 and the two radii the structured model retains genuine predictive power (MAE/std drops from 1.090 to 0.455 for

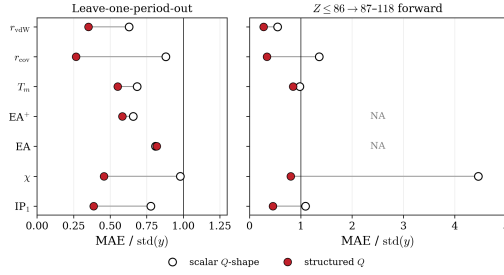


Figure 9. Paired error comparison for the scalar Q -shape baseline and the structured Q model. The left panel pools leave-one-period-out predictions; the right panel tests the independent $Z \leq 86 \rightarrow 87 - 118$ forward extrapolation. Open markers denote the scalar Q -shape baseline, and filled markers denote the structured Q model.

IP_1 with $R^2 = 0.53$, from 1.358 to 0.338 for r_{cov} with $R^2 = 0.83$, from 0.547 to 0.272 for r_{vdW} with $R^2 = 0.52$). For χ , MAE/std drops from 4.457 to 0.805, but the resulting $R^2 = -0.007$ means the structured prediction is essentially no better than the training-set mean on the 87 – 118 window. The reduction reflects the collapse of an extreme scalar baseline rather than true forward extrapolation of χ . All-EA remains worse in pooled LOPO, and the 54 $\rightarrow$ 86 transfer degrades several properties. Combining the in-sample LOPO comparison, the forward-holdout evidence, and the MJK-only ablation, the supported claim is that Q contributes real predictive value for IP_1 and the radii — most strongly for r_{cov} — while for χ , T_m and EA the observed structured-model improvements are largely inherited from the MJK combinatorial variables rather than from Q itself.

7.4 Ablation: contribution of Q beyond MJK combinatorial features

To isolate the added value of the analytic coordinate Q over the raw MJK combinatorial data (P , M , n , ℓ , `period_fill`, `sub_fill`, and one-hot ℓ), we retrain the structured model with all Q -dependent features removed (no Chebyshev trend in Q , no Fourier of $\text{frac } Q$, no interactions, no $\frac{dQ}{dZ}$), keeping only the MJK orbital block. All other choices — Huber loss,

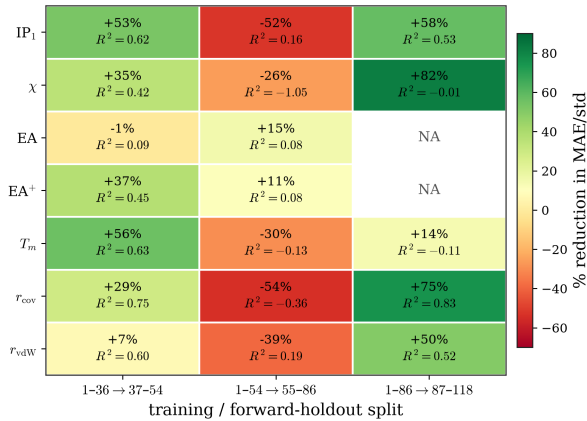


Figure 10. Forward-transfer landscape. Each cell reports the percentage reduction in MAE/std obtained by the structured Q model relative to the scalar Q -shape baseline, with the held-out R^2 printed below. Green cells improve; red cells worsen. The 54 → 86 column shows the main remaining limitation.

Ridge regularisation grid, transform selection, blocked cross-validation — are held fixed. Table 8 reports pooled leave-one-period-out and $Z \leq 86 \rightarrow 87 - 118$ forward-holdout metrics for both the full structured model (with Q) and the MJK-only ablation.

Property	Split	Structured MAE/std	Structured R^2	MJK-only MAE/std	MJK-only R^2
IP_1	LOPO	0.386	0.710	0.508	0.470
IP_1	forward	0.455	0.527	0.772	0.117
	86→118				
chi	LOPO	0.458	0.660	0.461	0.662
chi	forward	0.805	-0.007	1.188	-0.909
	86→118				
EA	LOPO	0.819	-0.230	0.734	-0.033
EA^+	LOPO	0.583	0.402	0.542	0.457
T_m	LOPO	0.552	0.320	0.578	0.295
T_m	forward	0.849	-0.108	0.717	0.217
	86→118				
r_{cov}	LOPO	0.266	0.874	0.473	0.625

Property	Split	Structured	Structured	MJK-only	MJK-only
		MAE/std	R^2	MAE/std	R^2
r_{cov}	forward	0.338	0.832	0.739	0.285
	86→118				
r_{vdW}	LOPO	0.351	0.719	0.378	0.705
r_{vdW}	forward	0.272	0.522	0.457	0.570
	86→118				

Table 8. MJK-only ablation. The MJK-only column reports the same predictive pipeline with all Q-dependent features removed (intercept + orbital block only). Lower MAE/std and higher R^2 are better. Q contributes clear predictive value over MJK-alone for IP_1 (LOPO 0.386 vs 0.508; forward 0.455 vs 0.772) and for r_{cov} (LOPO 0.266 vs 0.473; forward 0.338 vs 0.739), and a smaller improvement for r_{vdW} (LOPO 0.351 vs 0.378). For chi, T_m , EA and EA+ Q contributes little or nothing over MJK-only in LOPO; for T_m forward the MJK-only model is in fact better than the full structured model. This ablation supports a restricted claim: Q genuinely improves prediction where the residual periodic shape is coordinated across periods (IP_1 , radii); for properties dominated by chemical/structural idiosyncrasy (T_m) or by data-quality issues (EA), the added Q basis does not help.

The ablation therefore rules out the alternative reading that all the predictive value comes from the MJK combinatorial variables. For IP_1 and r_{cov} the improvement from adding Q-dependent features is large (LOPO MAE/std drop of 24–44%; forward MAE/std drop of 41–54%) and cannot be absorbed by expanding the MJK basis with the given tuning grid. Consistent with the periodicity-score results in Section 7.2, the properties for which Q genuinely helps are exactly those with the strongest residual-shape alignment in frac Q.

8 Comparison with Pettifor scale

Pettifor [28, 29] introduced a continuous chemical scale χ_P constructed empirically to maximise structural separation of binary compounds in two-dimensional maps. We compare $Q(Z)$ with χ_P on 103 common elements.

Proposition 8.1 (Q vs Pettifor weak rank correlation). *The Spearman rank correlation of $Q(Z)$ with Pettifor χ_P over 103 elements*

is $\rho = -0.240$. The Pearson correlation is $r = -0.393$. Pettifor ordering reorders elements by chemical scale, whereas Q preserves the analytic periodic-law progression in Z .

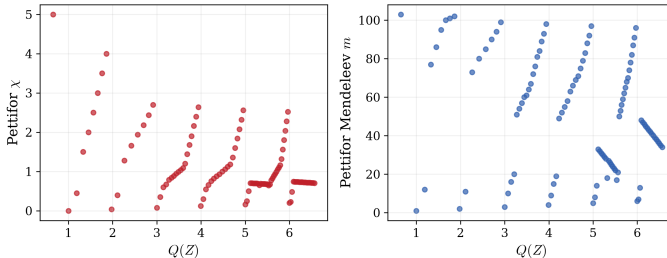


Figure 11. $Q(Z)$ vs Pettifor chi (left) and $Q(Z)$ vs Pettifor Mendelev number m_P (right) on 103 common elements. The low rank correlation indicates complementary orderings rather than orthogonality.

Empirical comparison on the six-property ensemble (Table 6) shows a mixed picture rather than a clean dominance: Q is the best-scoring coordinate for IP_1 (0.684) and r_{cov} (0.648), and competitive for r_{vdW} (0.758 vs grp/per 0.628). Mendelev m^* is best for chi (0.605) and T_m (0.708); grp/per is best for EA (0.540) and r_{vdW} (0.628). Pettifor χ^* is second-best for chi (0.709) but is never the top-scoring coordinate in this ensemble — in particular it is worse than Q for T_m (Pettifor 0.963 vs Q 0.827). This supports complementarity of the candidate coordinates rather than strict superiority of any one of them.

9 Predictive test and relativistic corrections

As a theoretical sanity check, the r_{cov} shape curve trained on $Z = 1..118$ is compared with eight superheavy DHF predictions of Pyykkö [30]. The bootstrap 95% CI covers the DHF values in 5 of 8 cases (62%), with mean absolute deviation 28 pm (14%). Because this fit uses the full known range, it is not treated as the main predictive validation; the independent forward-holdout results in §7.4 are the primary extrapolation evidence.

Proposition 9.1 (Four tested scalar relativistic variants do not improve the score). *For each of the four Sommerfeld-type correction*

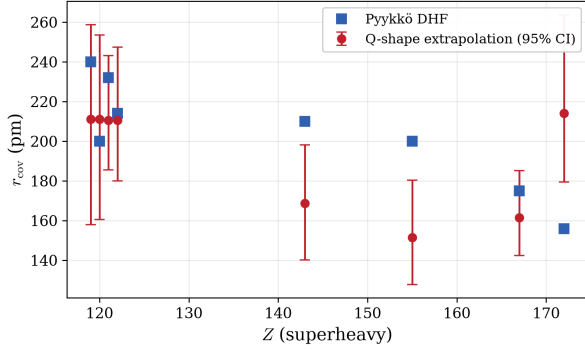


Figure 12. Q-shape extrapolation of r_{cov} for superheavy elements (red circles with 95% bootstrap CI) vs Pyykkö DHF predictions (blue squares). This is a theoretical sanity check against DHF tabulations, not an experimental validation.

functionals $\gamma_A(Z)$, $\gamma_B(Z)$, $\gamma_C(Z)$, and $\gamma_D(Z)$, the periodicity score $S(Q_{\text{rel}})$ with $Q_{\text{rel}} = \text{Rg}^{-1}(Z/\gamma)$ exceeds $S(Q_0 + Q_1)$ on all six tested properties.

This negative result is limited to four scalar rescalings and should not be interpreted as excluding more structured relativistic corrections. It is compatible with the idea that the leading periodic-law coordinate can remain useful before detailed relativistic shell effects are modelled explicitly.

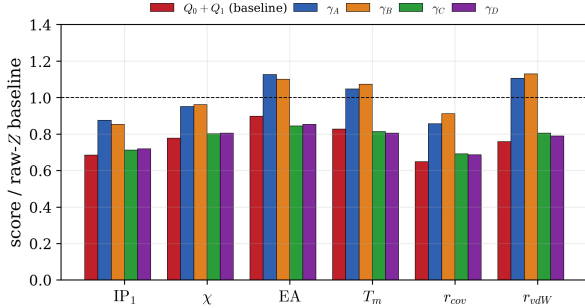


Figure 13. Periodicity score of $Q_0 + Q_1$ (red) and four simple Sommerfeld-type scalar variants $\gamma_A, \dots, \gamma_D$ on six properties. All four tested variants worsen the score for all properties.

10 Discussion and limitations

The rigorous framework of §§3–5 establishes $Q(Z)$ as an analytic periodic-law coordinate with proven existence, uniqueness, quadratic convergence, and axiomatic characterization. The asymptotic analysis connects the construction to the Thomas-Fermi-Tietz limit, while the Fourier, wavelet, and coherence analyses show how residual property shapes can be studied once the periodic coordinate has been fixed. Section 6 extends the same coordinate logic to electron-count variables for isoelectronic comparisons. The empirical sections then ask a separate question: how much of the observed tabulated periodicity is captured by scalar Q , and how far a structured Q /MJK model can be taken in prediction.

The main limitations are as follows. First, MJK has documented exceptions among the confirmed 118 elements, and Q inherits this idealized filling order. Second, scalar Q is not uniformly superior to Pettifor, Mendeleev, or grp/per baselines in direct prediction. Third, EA is strongly affected by source heterogeneity, nonpositive entries, and surrogate f-block values. Fourth, the structured Q model improves LOPO and the $Z \leq 86 \rightarrow 87 - 118$ holdout but worsens several $54 \rightarrow 86$ forward transfers, so its extrapolation value is property-dependent rather than universal. Fifth, the MJK-only ablation (§7.4, Table 8) sharpens this picture: the genuine incremental predictive contribution of Q over the raw MJK combinatorial variables is concentrated on IP_1 and the covalent radius (LOPO MAE/std reductions of 24% and 44% respectively; forward reductions of 41% and 54%), is marginal for r_{vdW} , and is essentially absent for χ , T_m and EA. The scientific claim of the paper is therefore restricted accordingly: Q is a productive analytic periodic coordinate for size- and valence-driven quantities, but does not replace chemistry-specific descriptors for structurally idiosyncratic properties such as T_m or noisy endpoints such as EA.

11 Conclusions and outlook

We have established the mathematical foundations of the analytic periodic-law coordinate $Q(Z)$: existence, uniqueness and real-analyticity of Q_0 ; closed-form Newton correction Q_1 ; local quadratic convergence with explicit Kantorovich bounds; axiomatic uniqueness of the smooth extension R_g among natural ansatz functions; asymptotic expansion coinciding at leading order with the Thomas-Fermi-Tietz limit; Fourier and Bochner analysis of residual shape curves; and an isoelectronic extension $Q_{\text{iso}}(Z, N)$. The empirical results support the following claim: scalar Q is a compact coordinate for periodic alignment, while a structured Q model using $\text{trend}(Q)$, circular $\text{frac } Q$, and MJK orbital variables gives strong improvements for IP_1 , radii, and several transfer tests. EA remains a weak endpoint, and some mid-heavy forward splits remain difficult. Future work should focus on structured Q -based descriptors, transparent data provenance, and principled relativistic/orbital corrections rather than on a universal one-dimensional predictor.

Data availability. All input data are taken from published tabulations cited in the reference list. Python code for reproducing the analyses and figures is available from the authors upon request.

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