

Explaining the Madelung Anomalies: From the Half-Filled-Shell Slogan to an Exchange-Counting Ladder

Maisara Shoeib¹

mshoeib@hct.ac.ae

Higher Colleges of Technology

Malak Torky²

Ahram Canadian University

Research Article

Keywords: Madelung rule, Aufbau anomalies, chemical explanation, exchange energy, periodic table, relativistic effects

Posted Date: October 14th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10261625/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Additional Declarations: No competing interests reported.

Explaining the Madelung Anomalies: From the Half-Filled-Shell Slogan to an Exchange-Counting Ladder

Maisara Shoeib^{1*}, Malak Torky²

¹ Master Analytical Chemistry, Higher Colleges of Technology (HCT), United Arab Emirates.

² Al-Ahram Canadian University, Cairo, Egypt.

***Corresponding author:** Maisara Shoeib

Email: mshoeib@hct.ac.ae

Co-author:

Malak Torky

Email: 42310427.Malak@acu.edu.eg

Abstract

Standard explanations of the Madelung/Aufbau anomalies often treat the twenty neutral-atom deviations as a flat exception list, with the half-filled-shell stability slogan offered as a general explanation. This paper argues that the issue is foundational rather than merely mnemonic: different cases require different kinds of chemical explanation. The anomalies are analysed as sign problems for pairs of competing configuration labels, not as a new configuration predictor. Eight 3d/4d sd cases (Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag) have an exact exchange-counting skeleton: promotion creates a same-spin pair increment ΔX that can be compared with standard promotion and Coulomb costs. Five cases (Pt, Au, Gd, Cm, Lr) form a mechanism-reduced class: scalar-relativistic frontier shifts, f7 exchange saturation, or 7p1/2 stabilization identify the direction, while numerical magnitudes require external relativistic input. The remaining seven early f/d cases (La, Ce, Ac, Th, Pa, U, Np) are self-consistent relativistic radial-ordering problems. In these cases the elementary sd-style exchange lever is no longer sign-decisive; in the hard f/d cases, f-shell exchange can oppose the observed transfer. A signed-threshold criterion identifies the Dirac-Fock, Dirac-Hartree-Fock, or multiconfiguration input needed for closure. The result replaces a single classroom slogan by a layered explanatory map: exchange-derived, mechanism-reduced, and relativistic-open cases.

Keywords: Madelung rule; Aufbau anomalies; chemical explanation; exchange energy; periodic table; relativistic effects

1. Introduction

Twenty neutral atoms between $Z = 24$ and $Z = 103$ occupy ground-state configurations that deviate from the Madelung ($n + \ell, n$) filling order: ten in the sd frontier of the transition rows, nine in the f/d frontier of the lanthanides and actinides, and one—lawrencium—at a relativistically shifted d/p edge. The difficulty is not only computational. It is also explanatory. Chemistry uses configuration labels as compact objects of reasoning, but the standard teaching route often turns a structured frontier problem into a memorized list of exceptions. The pedagogical literature has documented for decades that this treatment is unsatisfying, and that the standard classroom explanation is frequently wrong in detail (Scerri 1989; Wang et al. 2006; Schwarz 2010).

The standard explanation is the “half-filled-shell stability” slogan. Its appeal is understandable: it appears to work for chromium ($3d^5 4s^1$) and copper ($3d^{10} 4s^1$). But as a general chemical metaphor it fails twice over. First, it produces false positives: tungsten sits at exactly the same $d^4 \rightarrow d^5$ juncture as chromium and molybdenum, yet its ground state is $5d^4 6s^2$ —the half-filled configuration is not preferred. Second, it is silently transferred to cases it cannot address: lanthanum’s $5d^1 6s^2$ ground state involves no half-filled shell at all, and the early actinides (Th, Pa, U, Np) retain 6d occupancy for reasons that no shell-filling slogan reaches. A single explanation offered for twenty structurally different cases is a sign that the cases have not been classified.

This paper makes one claim: the twenty anomalies separate into three obstruction classes, distinguished by the kind of physical input needed to decide the sign of the configuration-energy difference. In Tier I (Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag), the sign-determining quantity is an exact combinatorial object—the same-spin pair increment ΔX created by an $s \rightarrow d$ transfer—multiplied by atomic exchange integrals that are standard Slater–Condon quantities (Condon and Shortley 1935; Racah 1942; Cowan 1981). Nothing in this tier is fitted; the combinatorics are exact and the integrals are tabulated or measurable, and in the chromium case the relevant exchange scale has in fact been measured spectroscopically (Zamudio-Bayer et al. 2015). In Tier II (Pt, Au, Gd, Cm, Lr), the operative mechanism is identified—scalar-relativistic 6s/5d shifts for Pt and Au, f7 exchange saturation for Gd and Cm, and spin–orbit stabilization of the $7p_{1/2}$ spinor for Lr (Xu and Pyykkö 2016)—but closing the magnitude requires relativistic input external to the elementary model. In Tier III (La, Ce, Ac, Th, Pa, U, Np), the elementary sd-style exchange-counting lever is no longer sign-decisive. In the hard f/d cases, exchange can even resist the observed transfer, so the sign is controlled by self-consistent relativistic radial ordering between compact f and diffuse d orbitals—a problem of a categorically different kind, requiring Dirac–Fock or multiconfiguration input (Desclaux 1973; Lu et al. 1973; Desclaux and Freeman 1978).

Three disclaimers bound the claim. This paper does not present a configuration predictor; it analyses the energy ordering behind labels that are already established (Kramida et al. 2024). It is not an ab initio calculation; where relativistic self-consistent input is required, the paper says so and specifies which quantity is missing rather than supplying a fitted surrogate. And it does not propose a single law covering all twenty cases; the central result is precisely that no such elementary law exists, because the cases belong to different obstruction classes. Identifying where an elementary derivation stops—and why it stops there—is presented as a positive result, not a concession.

1.1 Why this is a foundation-of-chemistry problem

The Madelung anomalies are a foundations-of-chemistry problem because they expose a tension between two legitimate explanatory demands. A full many-electron calculation may decide a configuration, but it does not automatically provide a compact chemical explanation. Conversely, a classroom slogan may be compact, but compactness is not explanation when it gives false positives, hides mechanism, or assigns one cause to structurally different cases.

The appropriate unit of explanation is therefore layered. Some cases can be explained by exact exchange counting plus standard atomic integrals; some can be reduced to a named mechanism whose magnitude is external; and some remain open to self-consistent relativistic calculation. This layered status is not a weakness of the analysis. It is the result: chemistry should not pretend that every exception is explainable at the same depth.

The half-filled-shell sentence is consequently treated here as a limited metaphor. Its legitimate kernel is exchange and exchange saturation. Its illegitimate extension is the claim that half-filled or closed subshells supply a universal rule. The ladder below separates the kernel from the overreach.

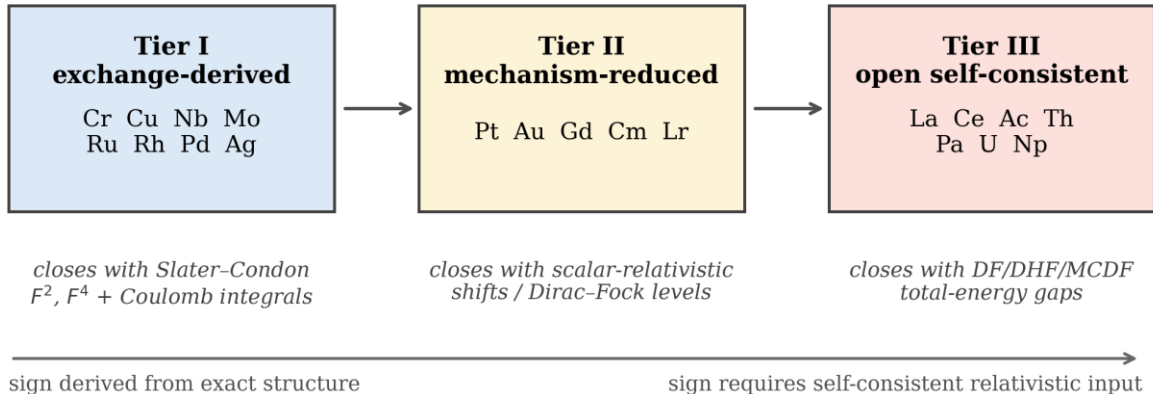


Figure 1. The anomaly-resolution ladder for the twenty Madelung deviations. Claim strength decreases from left to right: Tier I signs are derived from exact exchange counting, Tier II signs are supported by named mechanisms with external magnitudes, and Tier III signs require self-consistent relativistic input. The input that closes each tier is posted beneath it.

Terminology note. Throughout the paper, Tier I denotes exchange-derived cases, Tier II denotes mechanism-reduced cases, and Tier III denotes relativistic-open self-consistent cases. These names refer to the kind of input needed to settle the sign and scale of the competing configuration ordering; they are not labels of pedagogical importance or chemical complexity.

After this foundations framing, Section 2 states the sign problem and distinguishes anomaly resolution from label assignment. Section 3 develops the exchange-counting skeleton for the Tier I sd core, including the experimental exchange anchor for chromium and the tungsten negative control. Section 4 treats the five mechanism-reduced Tier II cases. Section 5 analyses the open Tier III frontier, derives a signed-threshold criterion that localizes the missing relativistic input, and explains through the orbital-collapse phenomenon why this tier is self-consistent rather than combinatorial. Section 6 discusses the explanatory, pedagogical, and research consequences of the classification.

2. The sign problem: label assignment versus anomaly resolution

An electron-configuration label is a compact statement about dominant occupancy. For the heavy and strongly mixed cases considered here, it is best read as a dominant-component spectroscopic descriptor rather than as an exact eigenstate: the true wavefunction near a frontier crossing is multiconfigurational, and the adopted labels in reference compilations are evaluated assignments attached to dominant configurations (Schwarz 2010; Kramida et al. 2024). This caution defines the status of the benchmark labels; it does not weaken them as data.

Two questions about these labels must be kept separate. *Label assignment* asks which configuration string should be attached to a given atom—a bookkeeping task that can be solved by lookup, by filling rules with exception lists, or by algorithmic selectors. *Anomaly resolution* asks a harder question: why does one near-degenerate configuration lie below another in energy? The second question is a sign problem. For two competing configurations A (the Madelung candidate) and B (the promoted or mixed candidate), the object of interest is

$$\Delta E = E(B) - E(A), \quad (1)$$

and the anomaly occurs exactly when $\Delta E < 0$. Every statement in this paper is a statement about the sign and, where possible, the scale of Equation (1) for a specific pair of configurations. No claim is made about absolute electronic energies, term splittings, fine structure, or correlated wave functions.

The distinction matters because the two questions have different success criteria. A label-assignment scheme is judged by agreement with a reference table, and agreement alone cannot distinguish physical insight from calibration: an exception list indexed by element name scores perfectly and explains nothing. Anomaly resolution is judged by whether the sign of Equation (1) follows from identifiable physics with identifiable inputs. The correct output of such an analysis is therefore not a single accuracy number but a classification: for each anomaly, either the sign is derived from exact structure plus standard integrals, or it is reduced to a named mechanism awaiting a magnitude, or it is localized to a specific missing calculation. The remainder of this paper constructs exactly that classification for the twenty Madelung deviations.

One further boundary should be stated at the outset. The analysis below uses non-relativistic exchange combinatorics where they are decisive (Tier I), names relativistic mechanisms where they are known (Tier II), and stops where the deciding quantity is a self-consistent relativistic fixed point (Tier III). Stopping is deliberate. Rigorous large- Z atomic-energy theory controls shell-averaged total energies, not the fixed- Z gap between two named configurations (Lieb and Simon 1977; Scott 1952; Fefferman and Seco 1994), and variational calculations supply upper bounds without matching lower bounds at the relevant 10^{-7} relative scale. Presenting a compact fitted coefficient as if it closed such a gap would misstate the evidence. The honest unit of progress here is the classification itself.

3. Tier I: the exchange-derived sd core

3.1 The exchange-counting skeleton

Consider a high-spin d^N subshell filled according to Hund's first rule. The number of same-spin electron pairs it contains is

$$X(N) = m(m-1)/2 + u(u-1)/2, \quad m = \min(N, 5), \quad u = \max(N-5, 0), \quad (2)$$

since for $N \leq 5$ every electron carries the same spin and the count is simply the number of pairs among N objects, while beyond half filling the second spin set opens and contributes its own pairs. For a one-electron $s \rightarrow d$ promotion, the exact exchange-pair gain is

$$\Delta X = X(N+1) - X(N). \quad (3)$$

This integer is not fitted, estimated, or calibrated. It is the combinatorial count of new parallel-spin $d-d$ pairs created by the promotion, and it is the exact part of the sd anomaly mechanism. Counting the pair and Coulomb changes between the Madelung candidate $A = ns^2(n-1)d^N$ and the promoted candidate $B = ns^1(n-1)d^{N+1}$ gives

$$\Delta E_{sd} = (\varepsilon_d - \varepsilon_s) - J_{ss} + (1-N)J_{sd} + NJ_{dd} - \Delta XK_{dd}, \quad (4)$$

where the J are average Coulomb integrals, K_{dd} is the average $d-d$ exchange integral—expressible through the standard Slater–Condon channels $F^2(nd, nd)$ and $F^4(nd, nd)$, or equivalently through Racah-type tabulations (Condon and Shortley 1935; Racah 1942; Cowan 1981)—and $(\varepsilon_d - \varepsilon_s)$ is the orbital promotion gap. The anomaly is favored when

$$\Delta XK_{dd} > (\varepsilon_d - \varepsilon_s) - J_{ss} + (1-N)J_{sd} + NJ_{dd}. \quad (5)$$

The division of labor in Equation (5) is the central structural point of this tier. The left side is exact combinatorics multiplied by a tabulated, and in one case measured, atomic integral. The right side is a promotion-plus-Coulomb cost built from standard atomic quantities. Nothing in the criterion refers to a configuration label, an element name, or a fitted decimal: the inputs are atomic-structure quantities, and the sign follows from their competition.

3.2 The eight cases

Table 1 records the exact pair counts for the eight Tier I anomalies. Chromium is the strong case: for $d^4 \rightarrow d^5$, $X(4) = 6$ and $X(5) = 10$, so $\Delta X = 4$ —the promotion creates four new same-spin exchange pairs, the largest one-electron gain available in a d shell. Ruthenium is the opposite limit inside the anomaly set: $d^6 \rightarrow d^7$ gives $\Delta X = 1$, the smallest nonzero increment, which matches its standing as the softest and most delicately balanced sd case. Palladium is a two-electron closure, $d^8 \rightarrow d^{10}$, evaluated as two sequential one-electron transfers with a net pair gain of 7 accompanied by full-shell closure.

Table 1. Exact same-spin-pair gain for the eight Tier I sd anomalies. The ΔX column is the derived combinatorial core of the mechanism; it involves no fitted quantity.

Element	Z	Transition	X_i	X_f	ΔX	Note
Cr	24	$3d^4 4s^2 \rightarrow 3d^5 4s^1$	6	10	4	half-shell gain; strongest one-electron case
Cu	29	$3d^9 4s^2 \rightarrow 3d^{10} 4s^1$	16	20	4	closure exchange gain
Nb	41	$4d^3 5s^2 \rightarrow 4d^4 5s^1$	3	6	3	moderate exchange gain
Mo	42	$4d^4 5s^2 \rightarrow 4d^5 5s^1$	6	10	4	half-shell exchange gain
Ru	44	$4d^6 5s^2 \rightarrow 4d^7 5s^1$	10	11	1	weakest exchange increment; softest case
Rh	45	$4d^7 5s^2 \rightarrow 4d^8 5s^1$	11	13	2	small exchange increment
Pd	46	$4d^8 5s^2 \rightarrow 4d^{10}$	13	20	7	two-electron closure case
Ag	47	$4d^9 5s^2 \rightarrow 4d^{10} 5s^1$	16	20	4	closure exchange gain

The same counting explains the non-cases, which is where the classification begins to pay for itself. For manganese and technetium, the candidate promotion $d^5 \rightarrow d^6$ carries $\Delta X = 0$: the sixth d electron begins the second spin set and creates no new parallel pair. There is no exchange drive at all, and the Madelung configuration stands. The half-filled-shell slogan gets these atoms right by accident; the pair count gets them right by construction.

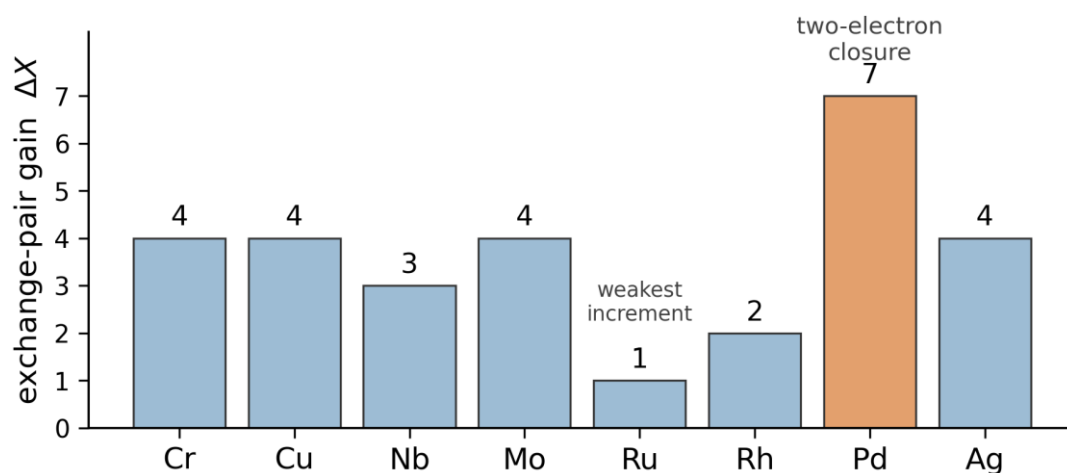


Figure 2. Exchange-pair gain ΔX for the eight Tier I sd anomalies, Equations (2)–(3). Ruthenium carries the weakest increment, matching its delicately balanced character; palladium is the two-electron closure with a net gain of 7. Not shown: Mn and Tc, whose candidate promotion carries $\Delta X = 0$ and which are regular.

3.3 The experimental exchange anchor

The exchange scale in Equation (5) is not confined to calculation. Zamudio-Bayer and co-workers identified the maximum-spin ground state of Cr_2^+ by x-ray magnetic circular dichroism and, through a Born–Haber analysis, used the atomic $4s^1 3d^5 \ ^7S-^5S$ spin-flip separation as a direct measure of the intra-atomic $3d-4s$ exchange scale; the reported separation is 0.94 eV (Zamudio-Bayer et al. 2015). This number is not used anywhere in the present analysis as a model coefficient. Its role is narrower and more valuable: it demonstrates that the exchange physics carrying the flagship chromium anomaly has a measurable spectroscopic anchor. The exact part of the mechanism is $\Delta X = 4$; the measured 0.94 eV supplies an external, laboratory-grade scale for the exchange integrals that this integer multiplies. The Tier I criterion is thereby tied at one end to combinatorics and at the other to spectroscopy, with tabulated Slater–Condon integrals bridging the remaining cases.

3.4 Tungsten as the negative control

A classification earns credibility by what it refuses to predict. Tungsten sits at exactly the same $d^4 \rightarrow d^5$ juncture as chromium and molybdenum, with the identical exchange increment $\Delta X = 4$, yet its ground state is $5d^4 6s^2$: the half-filled configuration loses. On the slogan account this is an embarrassment. On the account of Equation (5) it is expected: the criterion is an inequality, not a shell count. In the $5d$ row, scalar-relativistic stabilization of the $6s$ orbital raises the promotion cost ($\varepsilon_d - \varepsilon_s$) on the right side of the inequality faster than the $5d$ exchange integrals grow on the left (Pyykkö and Desclaux 1979; Pyykkö 2012). The same row dependence separates iron from ruthenium: both candidate promotions carry $\Delta X = 1$ at the $d^6 \rightarrow d^7$ step, yet iron retains $3d^6 4s^2$ while ruthenium promotes, because the $4d$ -row integrals and the $s-d$ gap differ from their $3d$ -row counterparts. ΔX fixes the exchange lever; the row fixes the scale it must overcome.

Where the row-dependent scale is itself dominated by relativity—platinum and gold in the $5d$ row—the case passes out of Tier I. Those atoms share the exchange-counting skeleton ($\Delta X = 3$ and 4 respectively) but their signs are settled only once scalar-relativistic frontier shifts are added. They open the mechanism-reduced tier, which is the subject of the next section.

4. Tier II: the mechanism-reduced cases

Five anomalies—Pt, Au, Gd, Cm, and Lr—occupy an intermediate evidentiary position. In each case the operative mechanism is identified, and the direction of the decision is understood, but closing the magnitude requires relativistic input that lies outside the elementary counting model. Placing these cases in their own tier prevents two opposite errors: presenting them as fully derived when their magnitudes are not, and lumping them with the genuinely open Tier III cases when their mechanisms are in fact settled.

4.1 Platinum and gold: exchange plus scalar relativity

Platinum ($5d^8 6s^2 \rightarrow 5d^9 6s^1$) and gold ($5d^9 6s^2 \rightarrow 5d^{10} 6s^1$) carry the same exchange-counting skeleton as the Tier I core, with $\Delta X = 3$ and $\Delta X = 4$ respectively, the latter a closure gain identical in structure to Cu and Ag. What removes them from Tier I is the row. In the $6s/5d$ frontier, scalar-relativistic effects shift both orbital energies at a scale comparable to the exchange terms themselves (Pyykkö and Desclaux 1979; Pyykkö 2012; Schwerdtfeger et al. 2020). The tungsten control of Section 3.4 showed one face of this: early in the row, relativistic $6s$ stabilization raises the promotion cost and the identical $\Delta X = 4$ lever fails to move the label. Late in the row the balance inverts: the d shell has descended across the series, the closure exchange gains are at their maximum, and the promoted configurations win. The sign of Equation (5) for Pt and Au is therefore settled only when scalar-relativistic ε_{6s} and ε_{5d} values are included alongside $F^2(5d, 5d)$ and $F^4(5d, 5d)$. The mechanism is not in doubt; the closure is quantitative, and its inputs are named.

4.2 Gadolinium and curium: exchange saturation at the half shell

The pair count of Equation (2) generalizes to a shell of arbitrary spatial degeneracy g :

$$X_g(N) = m(m-1)/2 + u(u-1)/2, \quad m = \min(N, g), \quad u = \max(N-g, 0), \quad (6)$$

with $g = 7$ for an f shell. Gadolinium and curium are then explained by the same zero that explained the Mn and Tc non-cases in Section 3.2, now acting on the f side of an f/d competition. The Madelung candidates are f^8s^2 ; the observed configurations are $f^7d^1s^2$. The decisive count is $\Delta X_f(7 \rightarrow 8) = X_f(8) - X_f(7) = 0$: the eighth f electron would begin the second spin set and gain no new same-spin f - f pair. The usual exchange advantage of continued f filling is therefore switched off at exactly this point, and a d^1 frontier electron becomes mechanistically natural. This is the legitimate core of the half-filled-shell intuition—stated as a vanishing exchange increment rather than as a stability slogan. What the counting does not supply is the magnitude of the f/d gap that the vanishing increment exposes; that requires relativistic $4f/5d$ and $5f/6d$ radial input of the kind tabulated in Dirac–Fock studies (Desclaux 1973; Lu et al. 1973; Desclaux and Freeman 1978). Gd and Cm are thus mechanism-reduced: the sign direction follows from exchange saturation, the scale from external relativistic data.

4.3 Lawrencium: the terminal relativistic d/p inversion

Lawrencium is the single d/p case, and it is the cleanest member of the tier because its mechanism is essentially a one-electron Dirac effect. The competing configurations are $6d^17s^2$ (the Madelung continuation) and the observed $7s^27p^1$. The relevant sign condition is

$$\Delta E_{dp} = \varepsilon^{rel}(7p_{1/2}) - \varepsilon^{rel}(6d) + \Delta E_{relax} + \Delta E_{corr} < 0, \quad (7)$$

driven by spin–orbit stabilization of the $7p_{1/2}$ spinor at $Z = 103$. This is not a qualitative slogan. Dirac–Fock calculations by Xu and Pyykkö (2016) show explicitly that the $7p^1$ ground configuration originates from relativity: remove relativity from the calculation and the valence electron occupies $6d^1$. The measured first ionization potential of lawrencium is consistent with this picture (Sato et al. 2015). No exchange-counting argument enters, and none is needed; the case is reduced to a documented differential self-consistent relativistic stabilization. What keeps Lr in Tier II rather than Tier I is that the deciding quantities are relativistic level energies, not combinatorics—the sign is anchored by published calculation and experiment, not derived from elementary structure.

The five Tier II cases share a common profile: a named mechanism, a settled direction, and a magnitude that is an input rather than a derivation. The remaining seven anomalies do not fit this profile. For them, the elementary sd-style exchange lever no longer survives as a sign-deciding rule, and no single chemical slogan or local pair count closes the case. The ordering is controlled by a self-consistent f/d radial problem.

5. Tier III: the relativistic-open self-consistent f/d frontier

5.1 Why the sd-style exchange lever no longer decides

The seven remaining anomalies—La, Ce, Ac, Th, Pa, U, and Np—differ from everything treated so far in one structural respect: their competing configurations move an electron between orbitals of different radial character, f and d . The simple sd question—how many new same-spin d–d pairs does an $s \rightarrow d$ promotion create?—is no longer the deciding question. In La and Ac no f -shell exchange is lost because the Madelung f occupation is only $f1$; in Gd and Cm the relevant $f8 \rightarrow f7d1$ comparison lies at the exchange-saturation boundary; but in Ce and the early actinides a transfer from f to d loses f -shell exchange while gaining little or no d -shell exchange. The elementary sd-style exchange lever is therefore not sign-decisive; in the hard f/d cases it can oppose the observed d participation.

$$\Delta E_{fd} = (\varepsilon_f - \varepsilon_d) + \Delta E_{Coul/ex} + \Delta E_{rel} + \Delta E_{corr}, \quad (8)$$

In this expression the frontier orbital-energy difference, the Coulomb–exchange rearrangement, the relativistic shift, and the differential correlation all enter at a scale comparable to the ordering gap itself. The task is therefore not to find a new half-filled-shell slogan. It is to determine a self-consistent radial and relativistic balance. Without

independent Dirac–Fock, Dirac–Hartree–Fock, or multiconfiguration input, any compact coefficient would be a calibration rather than a derivation.

5.2 A signed-threshold criterion

The tier can nevertheless be analysed further than a bare declaration of openness. Consider a local frontier transfer between the candidates $A = f^q d^r s^2$ and $B = f^{q-m} d^{r+m} s^2$. Using the generalized pair count of Equation (6), define the lost f -shell and gained d -shell same-spin exchange counts,

$$L_f = X_7(q) - X_7(q - m), \quad G_d = X_5(r + m) - X_5(r), \quad (9)$$

and normalize the frontier gap and the exchange-scale ratio by the average f - f exchange integral:

$$\delta = [\varepsilon_d^{rel} - \varepsilon_f^{rel} + \Delta E_{radial/corr/SO}] / K_{ff}, \quad \rho = K_{dd} / K_{ff}. \quad (10)$$

Setting the unevaluated residual terms to zero, the reduced ordering condition becomes

$$\Delta E_{fd} / K_{ff} = m\delta + L_f - \rho G_d, \quad (11)$$

so that the transfer is favored exactly when

$$\delta < \delta_{crit} = (\rho G_d - L_f) / m. \quad (12)$$

Equation (12) is a sign-and-threshold statement, not a derivation of any coefficient. Its value is that it separates the two roles cleanly: the numerator carries the signed exchange-transfer balance, which is exact combinatorics, while the denominator and δ carry the transfer normalization and the relativistic frontier gap, which are the genuinely missing inputs. Table 2 evaluates δ_{crit} for the nine activated f/d cases across a plausible range of the exchange ratio ρ . For a non-specialist reader, ρ should be read modestly: K_{dd} and K_{ff} are both average same-spin exchange scales built from Slater–Condon radial integrals of frontier d and f shells, so an order-one value such as $\rho = 1$ is a natural normalization point rather than a fitted claim. The additional values $\rho = 0.7$ and $\rho = 0.5$ deliberately bracket cases in which the d -shell exchange scale is smaller than the f -shell scale. Appendix A gives the exact angular expressions for both exchange averages; the grid brackets the physical scale rather than deriving it, and the gap-sign rows are independent of ρ altogether. G_d and C_m appear in the table for completeness; their vanishing L_f is precisely the exchange-saturation mechanism of Section 4.2, so the threshold formalism contains the Tier II f cases as its zero boundary.

Table 2. Signed-threshold analysis of the activated f/d cases. $\delta_{crit} = (\rho G_d - L_f)/m$. Negative thresholds mean the relativistic frontier gap must overcome lost f -shell exchange for the observed transfer to occur.

Z	El.	Frontier	m	L_f	G_d	$\rho = 1$	$\rho = 0.7$	$\rho = 0.5$	Class
57	La	$4f/5d$	1	0	0	0	0	0	gap-sign case
58	Ce	$4f/5d$	1	1	0	−1	−1	−1	hard fd ; lost f exchange
64	Gd	$4f/5d$	1	0	0	0	0	0	gap-sign (Tier II saturation)
89	Ac	$5f/6d$	1	0	0	0	0	0	gap-sign case
90	Th	$5f/6d$	2	1	1	0	−3/20	−1/4	bridge case
91	Pa	$5f/6d$	1	2	0	−2	−2	−2	hard fd ; MCDF/DHF needed
92	U	$5f/6d$	1	3	0	−3	−3	−3	hard fd ; MCDF/DHF needed
93	Np	$5f/6d$	1	4	0	−4	−4	−4	hard fd ; MCDF/DHF needed
96	Cm	$5f/6d$	1	0	0	0	0	0	gap-sign (Tier II saturation)

The table sorts the family into three classes. La, Ac, Gd, and Cm are gap-sign cases with $\delta_{crit} = 0$: any independently computed frontier gap favoring d occupation settles them, and no exchange bookkeeping stands in the way. Thorium, with $\delta_{crit} = (\rho - 1)/2$, is the clean bridge between gap-sign behavior and exchange-resistant transfer, because both L_f and G_d are nonzero; its threshold changes sign exactly at $\rho = 1$, so thorium is the single

case whose classification depends on the ratio of exchange scales itself—a further reason its closure requires extracted integrals rather than a bracketing grid. Ce, Pa, U, and Np carry increasingly negative thresholds: for them the relativistic gap must overcome one, two, three, and four units of lost f -shell exchange respectively, and only quantitative relativistic, correlation, relaxation, and spin–orbit input can decide the outcome. Published level-crossing calculations support the relevance of the $4f/5d$ and $5f/6d$ frontiers (Berengut et al. 2012), but tabulated one-electron reference data do not by themselves supply the competing-configuration total-energy differences or the K_{ff} and K_{dd} scales the criterion requires (Kotochigova et al. 1997). The classification is therefore stronger than a black-box statement—the sign structure is audited—but weaker than a coefficient derivation, and it says so.

The openness of the hard fd cases can be sharpened into quantitative targets without converting observed labels into a derivation. The adopted assignments place the promoted $f^{n-1}d$ configuration at the ground level; the question a closure calculation must answer is *by how much*. Evaluated level data fix the answer. The lowest observed level of the $f^n s^2$ competitor lies above the ground level by 4762.718 cm⁻¹ in Ce ($4f^2 6s^2 \ ^3H_4$), 12911.260 cm⁻¹ in Pa ($5f^3 7s^2$), 7020.709 cm⁻¹ in U ($5f^4 7s^2 \ ^5I_4$), and 2831 cm⁻¹ in Np ($5f^5 7s^2$)—approximately 0.59, 1.60, 0.87, and 0.35 eV respectively (Kramida et al. 2024; Blaise and Wyart 1992). These separations must not be read as sign closure: the sign is already part of the spectroscopic assignment that defines each anomaly, and restating it proves nothing. Their role is stricter. They are empirical magnitude targets that any successful Dirac–Fock, multiconfiguration, or relativistic-correlation treatment of the negative thresholds in Table 2 must reproduce while paying the listed L_f units of lost f -shell exchange.

The trend across these targets is itself diagnostic. The exchange-resistance ladder increases monotonically— $L_f = 1, 2, 3, 4$ for Ce, Pa, U, and Np—yet the observed competitor gaps in the actinide sequence decrease from Pa (1.60 eV) through U (0.87 eV) to Np (0.35 eV). If exchange counting were the controlling physics of this tier, neptunium would be the hardest case; instead it is the closest to reversal. The radial-relativistic stabilization of the promoted $f^{n-1}d$ branch evidently grows across the actinide sequence faster than the internal f -exchange resistance, until the ordering inverts at plutonium, where $5f^6 7s^2$ is again the ground configuration and the lowest $5f^6 6d 7s^2$ level lies 6313.866 cm⁻¹ above it (Kramida et al. 2024). The hard fd sector is therefore not an unresolved exception list. It is a set of measured magnitude targets, arranged along a monotone trend that terminates in a sign reversal at Pu—exactly the behavior expected of a deepening self-consistent f collapse, and exactly the behavior an exchange-counting account cannot produce.

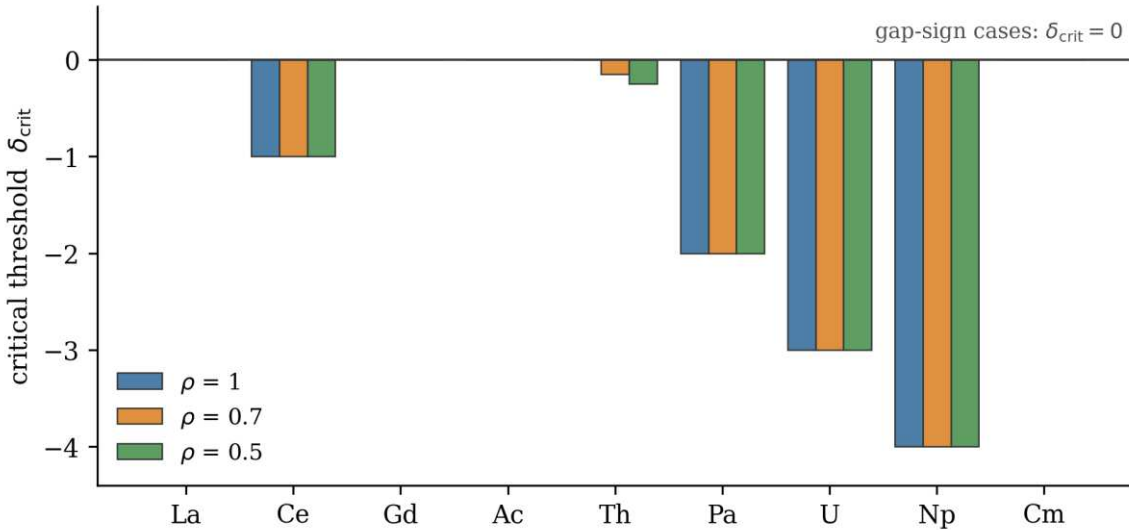


Figure 3. Signed-threshold ladder for the activated fd cases, Equation (12), at three values of the exchange ratio ρ . La, Gd, Ac, and Cm are gap-sign cases with $\delta_{crit} = 0$. Thorium is the bridge case, $\delta_{crit} = (\rho - 1)/2$. Ce, Pa, U, and Np require increasingly negative frontier gaps because transfer loses f -shell same-spin exchange.

5.3 The self-consistent barrier: orbital collapse and the limits of rigor

Why can the missing δ not be supplied by an elementary estimate? The obstruction is physical and structural. An electron of angular momentum ℓ in an effective atomic field moves in

$$V_{\text{eff}}(r) = -Z_{\text{eff}}(r)/r + \ell(\ell + 1)/2r^2, \quad (13)$$

and for $\ell = 3$ the centrifugal term is large enough to separate an inner well from an outer well. Across the lanthanide and actinide onsets, the $4f$ or $5f$ orbital crosses from an outer, valence-like state to a compact, core-like state—the orbital-collapse phenomenon with a long history in rare-earth atomic physics (Goeppert-Mayer 1941; Connerade 1998). The sign of $(\varepsilon_f - \varepsilon_d)$ depends on which side of that collapse the atom occupies. But $Z_{\text{eff}}(r)$ depends on the very occupancy whose ordering is being decided: the deciding quantity is a fixed point of a self-consistent atomic problem, not an explicit function of Z alone. This is the precise sense in which Tier III is a different obstruction class. Dirac–Fock, Dirac–Hartree–Fock, and multiconfiguration calculations are the natural tools for that input (Desclaux 1973; Lu et al. 1973; Desclaux and Freeman 1978; Grant 2007; Froese Fischer et al. 2007), and nothing lighter substitutes for them.

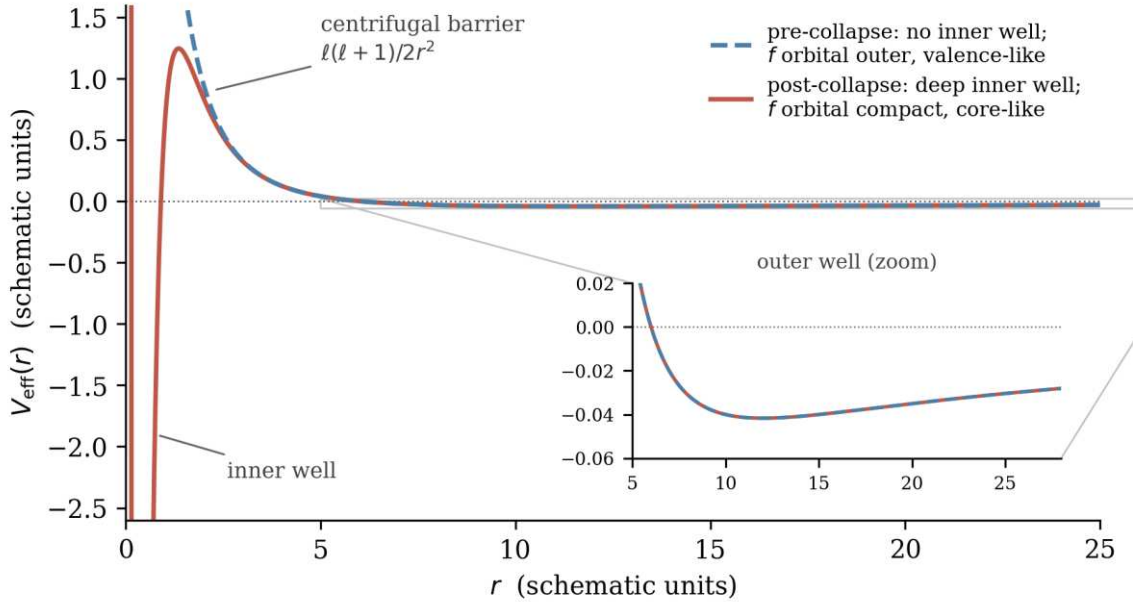


Figure 4. Schematic effective potential for an $\ell = 3$ electron, Equation (13), with $Z_{\text{eff}}(r) = 1 + (Z - 1)e^{-ar}$. Both curves share the centrifugal barrier and the shallow outer well (inset); only the post-collapse curve develops a deep inner well. The sign of $(\varepsilon_f - \varepsilon_d)$ depends on which side of the collapse the atom occupies, and Z_{eff} itself depends on the occupancy being decided—the Tier III fixed-point obstruction.

It is equally important to state what rigorous theory does not currently reach, so that the openness of the tier is not mistaken for a lack of effort. Large- Z atomic-energy theory controls a smooth approximation to the *total* ground-state energy through the Thomas–Fermi term, the Scott correction, and the Dirac–Schwinger correction (Lieb and Simon 1977; Scott 1952; Fefferman and Seco 1994). For cerium, the smallest rigorously controlled term is of order $Z^{5/3} \approx 8.7 \times 10^2$ atomic units, while a representative f/d ordering difference is of order 0.05 eV $\approx 1.8 \times 10^{-3}$ atomic units—a separation of roughly five orders of magnitude between what the theorems bound and what the anomaly requires. This comparison is a scale indicator, not an impossibility proof: the asymptotic theorems address a different object than the fixed- Z shell-resolved gap. Computationally, the total electronic energy of a heavy atom is of order 10^4 atomic units, so proving the sign of a 10^{-3} -atomic-unit gap demands two-sided bounds at a relative precision of about 10^{-7} ; variational methods supply upper bounds, but matching lower bounds of that quality are not available for correlated relativistic open-shell atoms, and in the heaviest cases the no-pair formulation adds its own layer of model dependence through the Brown–Ravenhall difficulty (Brown and

Ravenhall 1951). None of this is a reason to distrust Dirac–Fock or multiconfiguration calculations as practical tools. It is a reason to classify Tier III as open with respect to elementary and rigorous derivation, and to name the calculation that closes each case rather than papering over the gap with a fitted number.

6. Discussion

6.1 The classification at a glance

Table 3 collects the result. The twenty anomalies resolve into eight Tier I exchange-derived cases whose sign follows from exact combinatorics competing against standard atomic integrals; five Tier II mechanism-reduced cases whose direction is supported by a named mechanism but whose magnitudes require external input; and seven Tier III relativistic-open self-consistent cases where the decisive quantity is a frontier radial-ordering calculation rather than an elementary exchange count.

Table 3. The anomaly-resolution ladder. Each tier is characterized by what is established and by the external input required to close its remaining magnitudes or signs.

Tier	Cases	What is established	Input needed to close
I	Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag	exact ΔX skeleton; sign from the exchange–cost inequality of Eq. (5); chromium anchored by a measured 0.94 eV exchange scale	Slater–Condon F^2 , F^4 and Coulomb integrals; s/d orbital gaps
II	Pt, Au, Gd, Cm, Lr	mechanism named and direction supported: scalar-relativistic frontier shifts; f7 exchange saturation ($\Delta X_f = 0$); relativistic 7p1/2 stabilization	external scalar-relativistic $\epsilon 6s$, $\epsilon 5d$ and F_2 , $F_4(5d)$ inputs; relativistic f/d radial magnitudes; Dirac–Fock level energies for Lr
III	La, Ce, Ac, Th, Pa, U, Np	elementary sd-style exchange counting is not sign-decisive; obstruction localized to self-consistent relativistic f/d radial ordering; sign structure audited by Eq. (12)	DF/DHF or MCDF competing-configuration total-energy gaps; extraction of K_{ff} and K_{dd} scales

6.2 Pedagogical consequences

The classification supplies a direct replacement for the half-filled-shell slogan, at the same level of classroom effort but without its failures. Three teachable statements carry the content. First, the driver of the Cr-type anomalies is a countable object: promotion is favored when the new same-spin pairs it creates, ΔX , buy enough exchange energy to pay the promotion cost—an inequality, not a shell count. The same counting explains the regular atoms: Mn and Tc do not promote because $\Delta X = 0$ at the $d^5 \rightarrow d^6$ step, and tungsten does not promote because the 5d-row cost outruns an identical $\Delta X = 4$ gain. Second, the legitimate kernel of the half-shell intuition is exchange saturation, and its correct application is Gd and Cm, where $\Delta X_f(7 \rightarrow 8) = 0$ switches off the advantage of continued f filling. Third, the La-type cases are not half-shell stories at all and should not be taught as such; they belong to relativistic self-consistent atomic structure, and an honest classroom statement is that their explanation lives at the Dirac–Fock level (Schwarz 2010; Schwerdtfeger et al. 2020). Students lose a slogan and gain a mechanism, a counterexample, and a truthful boundary.

6.3 The half-filled-shell slogan as a limited metaphor

For a foundations-of-chemistry reading, the important point is not merely that the slogan has counterexamples. Many useful chemical expressions have limited domains. The problem is that the half-filled-shell slogan is often used without stating its domain. In the present classification, “half-filled stability” is acceptable only when translated into a specific exchange or exchange-saturation statement. It is not acceptable as a universal causal rule.

Chromium, gadolinium, tungsten, lanthanum, and uranium should not be forced into the same explanatory sentence.

6.4 Research consequences

For the atomic-structure community, the ladder converts a folklore topic into an executable task list. Tier I invites a systematic tabulation: element-resolved $F^2(nd, nd)$, $F^4(nd, nd)$, Coulomb integrals, and s/d gaps inserted into Equation (5) would close all eight magnitudes with no free parameters, and any failure would be informative. Tier II requires scalar-relativistic orbital energies that existing Dirac–Fock tabulations already largely contain (Desclaux 1973; Lu et al. 1973). Tier III is the substantive target: competing-configuration total-energy differences at the DF/DHF or MCDF level for the seven listed atoms, together with extracted K_{ff} and K_{dd} scales, would decide the negative thresholds of Table 2 case by case against the measured 0.35–1.60 eV level separations recorded in Section 5.2. These are bounded, well-posed calculations for modern relativistic codes (Grant 2007; Froese Fischer et al. 2007), and the analysis states in advance exactly what each result would confirm or refute—it is falsifiable at the level of signs before any coefficient is fitted, and at the level of magnitudes once the targets are in view.

Two boundaries of the present analysis deserve restating. The configuration labels analysed here are dominant-component spectroscopic descriptors adopted from an evaluated compilation (Kramida et al. 2024); near frontier crossings the true states are multiconfigurational, and nothing in the ladder depends on pretending otherwise. And the ladder is not a prediction engine: it neither assigns labels nor competes with electronic-structure calculation. It organizes the explanatory landscape of twenty known facts, and its claims are confined to the sign and scale structure of Equation (1).

7. Conclusion

The twenty Madelung anomalies are not one problem wearing twenty faces. Eight Tier I cases are decided by an exact combinatorial exchange increment competing against a standard promotion cost, with the flagship chromium case tied to a measured spectroscopic exchange scale. Five Tier II cases are mechanism-reduced cases: the relevant exchange saturation or relativistic mechanism is identified, but numerical closure requires external input. Seven Tier III cases remain relativistic-open self-consistent f/d problems, where the exchange-resistance target can be written but not closed without Dirac–Fock, Dirac–Hartree–Fock, or multiconfiguration calculations. The classification demonstrates that a mature chemical explanation must be multi-layered, acknowledging the limits of elementary models without abandoning their usefulness.

Data availability

Supplementary Python scripts, generated tables, figures, console logs, and reproducibility outputs are provided with the submission. The scripts regenerate the exchange-counting tables, signed-threshold calculations, Wigner-3j exchange-average coefficients, and figure files from declared case-input definitions and explicitly stated equations.

Author contributions

Maisara Shoeib: Conceptualization, methodology, formal analysis, investigation, writing – original draft, writing – review and editing, visualization.

Malak Torky contributed to the supplementary Python development and implementation, code review, reproducibility checking, figure generation, and formatting of the computational outputs used in the manuscript and Supplementary Information.

Both authors reviewed the final manuscript and approved its submission.

Declaration of Competing Interest

The authors declare no competing interests.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declaration of generative AI use

During the preparation of this work, the author used AI assistants (Claude, Anthropic; ChatGPT, OpenAI) for language editing, structural revision, and consistency checking. The author reviewed and edited all AI-assisted output, verified the scientific content and all numerical values, and takes full responsibility for the final manuscript.

Appendix A: Average same-spin exchange integrals

The quantities K_{dd} in Equation (4) and K_{ff} , K_{dd} in Equation (10) are average same-spin exchange integrals over a high-spin shell. For equivalent electrons nl , the exchange integral between spatial orbitals m and m' is $K(m, m') = \Sigma_k [c^k(lm, lm')]^2 F^k$, with the standard Condon–Shortley angular coefficients built from Wigner 3- j symbols. Averaging over all unordered pairs of the shell gives, exactly,

$$\bar{K}_{dd} = (2/35) F^2(nd, nd) + (4/63) F^4(nd, nd), \quad (A1)$$

$$\bar{K}_{ff} = (8/225) F^2(nf, nf) + (8/297) F^4(nf, nf) + (200/5577) F^6(nf, nf). \quad (A2)$$

These rational coefficients are exact angular results, evaluated by direct Wigner-3j summation in the companion script. They are included to make the exchange-counting layer auditable, not to convert the whole ladder into an ab initio calculation. Two checks anchor them. Internally, combining the pair averages of Equations (A1)–(A2) with the trace sum rule for the direct anisotropies ($\Sigma_k c^k(lm, lm) = 0$ for $k > 0$) reproduces the classical Condon–Shortley energy of the half-filled d shell, $E(d5\ 6S) = 10F0 - 35F2 - 315F4$, exactly (Condon and Shortley 1935). Externally, representative Hartree–Fock-scale Slater integrals place both averages at a few tenths of an electronvolt and their ratio $\rho = \bar{K}_{dd}/\bar{K}_{ff}$ near unity, consistent with the range spanned in Table 2; on the same averages, a single spin flip in f7 breaks six parallel pairs and costs roughly 3.5 eV, the observed scale of the Gd3+ 8S–6P separation. With tabulated F_k values, every quantity in Equations (5), (10), and (12) is therefore computable without free parameters, but Tier III still requires independent relativistic radial and correlation input.

References

- Berengut JC, Dzuba VA, Flambaum VV, Ong A (2012) Highly charged ions with E1, M1, and E2 transitions within laser range. *Phys Rev A* 86:022517
- Blaise J, Wyart J-F (1992) *Selected Constants: Energy Levels and Atomic Spectra of Actinides*. Tables Internationales de Constantes, Paris
- Brown GE, Ravenhall DG (1951) On the interaction of two electrons. *Proc R Soc A* 208:552–559
- Condon EU, Shortley GH (1935) *The Theory of Atomic Spectra*. Cambridge University Press, Cambridge
- Connerade J-P (1998) *Highly Excited Atoms*. Cambridge University Press, Cambridge
- Cowan RD (1981) *The Theory of Atomic Structure and Spectra*. University of California Press, Berkeley
- Desclaux JP (1973) Relativistic Dirac–Fock expectation values for atoms with $Z = 1$ to $Z = 120$. *At Data Nucl Data Tables* 12:311–406
- Desclaux JP, Freeman AJ (1978) Dirac–Fock studies of some electronic properties of actinide ions. *J Magn Magn Mater* 8:119–129
- Fefferman C, Seco L (1994) On the Dirac and Schwinger corrections to the ground-state energy of an atom. *Adv Math* 107:1–185
- Froese Fischer C, Tachiev G, Gaigalas G, Godefroid MR (2007) An MCHF atomic-structure package for large-scale calculations. *Comput Phys Commun* 176:559–579
- Goeppert-Mayer M (1941) Rare-earth and transuranic elements. *Phys Rev* 60:184–187
- Grant IP (2007) *Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation*. Springer, New York
- Kotochigova S, Levine ZH, Shirley EL, Stiles MD, Clark CW (1997) Atomic Reference Data for Electronic Structure Calculations. NIST Standard Reference Database 141. National Institute of Standards and Technology
- Kramida A, Ralchenko Yu, Reader J, NIST ASD Team (2024) NIST Atomic Spectra Database, version 5.12. NIST Standard Reference Database 78. National Institute of Standards and Technology
- Lieb EH, Simon B (1977) The Thomas–Fermi theory of atoms, molecules and solids. *Adv Math* 23:22–116
- Lu CC, Carlson TA, Malik FB, Tucker TC, Nestor CW (1973) Self-consistent relativistic Dirac–Hartree–Fock calculations of lanthanide atoms. *At Data Nucl Data Tables* 5:201–229
- Pyykkö P (2012) The physics behind chemistry and the periodic table. *Chem Rev* 112:371–384
- Pyykkö P, Desclaux J-P (1979) Relativity and the periodic system of elements. *Acc Chem Res* 12:276–281
- Racah G (1942) Theory of complex spectra. I. *Phys Rev* 61:186–197
- Sato TK, Asai M, Borschevsky A, et al. (2015) Measurement of the first ionization potential of lawrencium, element 103. *Nature* 520:209–211

- Scerri ER (1989) Transition metal configurations and limitations of the orbital approximation. *J Chem Educ* 66:481
- Schwarz WHE (2010) The full story of the electron configurations of the transition elements. *J Chem Educ* 87:444–448
- Schwerdtfeger P, Smits OR, Pykkö P (2020) The periodic table and the physics that drives it. *Nat Rev Chem* 4:359–380
- Scott JMC (1952) The binding energy of the Thomas–Fermi atom. *Philos Mag* 43:859–867
- Wang SG, Qiu YX, Fang H, Schwarz WHE (2006) The challenge of the so-called electron configurations of the transition metals. *Chem Eur J* 12:4101–4114
- Xu W-H, Pykkö P (2016) Is the chemistry of lawrencium peculiar? *Phys Chem Chem Phys* 18:17351–17355
- Zamudio-Bayer V, Hirsch K, Langenberg A, et al. (2015) Maximum spin polarization in chromium dimer cations as demonstrated by x-ray magnetic circular dichroism spectroscopy. *Angew Chem Int Ed* 54:4498–4501

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [MadelungLadderSupplementaryCodeandFigures.zip](#)