

Ionization Energy Without Differencing: Two Columns from the Radius of the Ion That Remains

Claes Johnson¹

¹KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden ,
claesjohnson@gmail.com

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Abstract

A first ionization energy is a small difference of large quantities: for potassium it is 0.027% of the total electronic energy. No method whose totals carry a per-cent residual can obtain it by differencing two solves, since the signal falls below the error bar on each. This is why the standard formalism computes ionization by dedicated machinery rather than by subtracting ground-state energies, and why a continuum model of the atom accurate to one or two per cent on totals is silent on ionization if asked the question that way. We report a construction that does not ask it that way. Screening the core to its net charge $+V$ and giving the valence its own domain outside a radius R , with a free boundary at R , makes the core energy cancel *analytically* rather than numerically. The resulting quantity is a one-electron problem whenever only one valence density is present — the first ionization energy of an alkali, the *second* of an alkaline earth — and is then free of the over-separation that a hard partition between two densities introduces. Compared in each case against the radius of the ion that remains, one constant per column reproduces ten measured ionization energies: the alkalis to 1.4% about $k = 0.967$ and the alkaline earths to 3.6% about $k = 1.101$, in both cases with the column's first and smallest member deviating by some 17% — lithium at 1.171, beryllium at 1.169, the same amount in the same direction. Both constants are within a tenth of unity: the radius the construction needs is the radius crystallography assigns the remaining ion. The relation has a boundary — the remaining ion must carry a closed noble-gas core, and group 13 fails — and two honest limits. The ionic radius is supplied, and is itself a conventional split of measured distances whose 14 pm of convention is the size of the effect, so this is a correlation between two measurements rather than a prediction from Z . And the model can supply the radius itself, as it does for lithium to 5%; what blocks it elsewhere is one measured defect, an excess of 1.67 a.u. of interface radius per core shell.

1 The arithmetic that forbids differencing

Write $IE = E(\text{ion}) - E(\text{atom})$. Both terms are large and nearly equal. Table 1 gives the fraction of the total that the difference represents, together with what a 1.6% residual on the total — the mean error of the continuum model of [6] across the first three periods — amounts to in the same units.

From boron onward the quantity sought is smaller than the uncertainty on the quantities it is extracted from. At sodium it is one fourteenth of that uncertainty; at potassium one fiftieth. The conclusion does not depend on which model supplies the totals. It is arithmetic, and it applies to any method with a per-cent residual.

Table 1: A first ionization energy as a fraction of the total electronic energy it would have to be differenced out of, and the signal-to-error-bar ratio at a 1.6% residual on totals. Measured values from [1].

	$ E_{\text{tot}} $ (Ha)	IE (Ha)	IE/ $ E_{\text{tot}} $	signal/error bar
He	2.903	0.9036	31.1%	19.4
Li	7.478	0.1981	2.65%	1.66
Be	14.667	0.3425	2.34%	1.46
B	24.654	0.3049	1.24%	0.77
C	37.845	0.4138	1.09%	0.68
N	54.589	0.5341	0.98%	0.61
O	75.067	0.5001	0.67%	0.42
F	99.734	0.6403	0.64%	0.40
Ne	128.94	0.7925	0.62%	0.38
Na	162.25	0.1886	0.116%	0.07
K	599.16	0.1595	0.027%	0.02

Two consequences follow. The first is that the standard formalism’s practice is not a historical accident: Koopmans’ theorem, ΔSCF , equation-of-motion coupled cluster and GW exist because ionization is computed by machinery built for it, not by subtracting two ground-state energies [3, 4, 5]. The second is that a model reporting totals to one or two per cent, and declining to report ionization energies, is not thereby incomplete in a way the totals conceal — it is declining to divide a number by something smaller than its own error bar.

ΔSCF nevertheless succeeds where the core is nearly unchanged between the two solves, because then most of the error cancels between them. The construction below makes that cancellation exact instead of accidental.

2 The construction

Let the atom have V valence electrons outside a closed core of $Z - V$ electrons. Replace the core by its net charge, a kernel of charge $+V$, and let the valence densities occupy the region outside a radius R . Writing $E_{\text{val}}(n)$ for the energy of n such densities on that kernel,

$$\text{IE} = E_{\text{val}}(V - 1) - E_{\text{val}}(V), \quad (1)$$

and the core energy is absent from both terms rather than subtracted between them. For $V = 1$ this reduces to $\text{IE} = -E_{\text{val}}(1)$: the ionization energy *is* the valence electron’s energy, and no difference is formed at all.

The electron obeys

$$-\frac{1}{2}\nabla^2 u - \frac{V}{r}u = \varepsilon u, \quad r > R, \quad (2)$$

with the *free* (homogeneous Neumann) condition $\partial u / \partial n = 0$ at $r = R$, free at infinity, normalised to one electron. The condition at R is the model’s own: the interface between core and valence is a free boundary, not a node, so nothing is imposed on u there and the natural condition follows from the functional. As $R \rightarrow 0$ the exterior energy must rise above hydrogen’s by about $2R^2$, the potential lost in excising $r < R$; at $R = 0.05$ the solve gives 0.4957 against that estimate’s

0.4950, so the free condition approaches the hydrogen limit correctly and from the physical side. Imposing $u(R) = 0$ instead halves the fitted radius and loses the result of Section 3. For $V > 1$ the valence densities are non-overlapping, so (1) is a difference within one composition, taken on one kernel, with the core absent from both sides.

The check in which nothing can be adjusted, and the case it does not cover. At $R = 0$ the construction has no freedom whatever. For $V = 1$ it is hydrogen, and (2) returns -0.5 analytically. That is the anchor, and it is exact rather than fitted.

For $V = 2$ the same limit is less kind, and the reason bears on everything that follows. At $R = 0$ with a kernel of $+2$, equation (1) is the full two-electron problem: helium, with its two valence densities occupying disjoint domains. Solved to convergence that construction gives $E = -3.026$ Ha, so

$$\text{IE} = E(\text{He}^+) - E(\text{He}) = -2.000 - (-3.026) = 1.026,$$

against a measured 0.9036 — high by 14%. The cause is known and is not the radius: two densities confined to disjoint domains avoid each other *completely and permanently*, which is more avoidance than Coulomb correlation produces, so the pair repulsion comes out some four per cent low and the state over-binds. A value of 0.903 has been reported for this case [7]; it is a value the imaginary-time relaxation passes through on its way — driving that computation to its own stopping point shows the energy rising monotonically through -2.903 at about two thousand steps and reaching -2.826 by three thousand, still rising — and not the limit of the construction.

Which ionization energies are one-electron quantities. The defect just described requires two valence densities to partition against one another, so the quantities to trust are those for which (1) involves only one. Writing out the $V = 2$ case,

$$\text{IE}_1 = E_{\text{val}}(1) - E_{\text{val}}(2), \quad \text{IE}_2 = E_{\text{val}}(0) - E_{\text{val}}(1) = -E_{\text{val}}(1),$$

and the double ionization $\text{IE}_1 + \text{IE}_2 = -E_{\text{val}}(2)$. The *second* ionization energy of an alkaline earth is therefore a one-electron problem — no partner, no interface, no over-separation — while its first is not, and the double ionization is not. The clean family is accordingly

one electron on a kernel of charge V , against the radius of the ion that remains:

$$V = 1 : \text{IE}_1(\text{alkali}) \text{ vs } r(\text{M}^+); \quad V = 2 : \text{IE}_2(\text{alkaline earth}) \text{ vs } r(\text{M}^{2+}); \quad V = 3 : \text{IE}_3 \text{ vs } r(\text{M}^{3+}).$$

Each member is equation (2) with a different V , and in each the only approximation is that the core has been replaced by its net charge at radius R .

The outer boundary must be removed. Earlier numerical realisations confined the valence density to an annulus $R < r < 5$ a.u. [9], while the two-valence realisation [10] limits it only by the box; the two are therefore not on the same footing. That second length does real work: solved on $R < r < \infty$ instead, the energy at $R = 1.6$ changes from 0.196 to 0.1447 Ha. Since the inner radius is the quantity of interest, the outer cutoff must go, and with it the only other length in the problem. Equation (2) on $R < r < \infty$ is well posed, and we solve it as a radial eigenvalue problem converged to 10^{-8} .

Table 2: The radius required to reproduce each measured first ionization energy, against the ion’s measured six-coordinate radius [2]. Crystal scale, $r(\text{O}^{2-}) = 126$ pm, which Shannon states corresponds more closely to the physical size of ions in a solid. The ratio is unity to within a few per cent from sodium to caesium: the radius the construction requires *is* the measured radius of the ion that remains.

	IE (Ha)	R_{fit} (a.u.)	r_{ion} (a.u.)	$R_{\text{fit}}/r_{\text{ion}}$
Li	0.19814	1.9915	1.7008	1.171
Na	0.18886	2.1540	2.1921	0.983
K	0.15952	2.8044	2.8724	0.976
Rb	0.15351	2.9711	3.1369	0.947
Cs	0.14310	3.2956	3.4204	0.964
mean, Na–Cs				0.967
standard deviation, Na–Cs				1.4%
lithium				1.171

3 One constant per column

Table 2 inverts (2) for each alkali: the radius at which the computed energy equals the measured ionization energy. The question is then whether those radii are anything, or merely five numbers fitted to five numbers.

They are not five free numbers, and the ratio is not an arbitrary one. **The required radius equals the measured radius of the ion.** Fixing the single constant once on sodium through caesium, $k = 0.967$, and computing with no per-atom adjustment:

$$R = 0.967 r_{\text{ion}} \implies \frac{\text{IE}_{\text{comp}}}{\text{IE}_{\text{meas}}} = 1.01, 1.01, 0.99, 1.00 \quad (\text{Na, K, Rb, Cs}), \quad (3)$$

a maximum deviation of 1.4% and a mean of 0.8%. Lithium, computed with the same constant, comes out at 1.12 — a 12% deviation, reported rather than absorbed.

That k is unity to within three per cent is the substance of the result. The claim is not that some fraction of an ionic radius can be tuned to fit; it is that the radius at which the valence density must be cut off, for the model to return the measured ionization energy, is the radius crystallography measures for the ion that remains. Nothing is left to adjust between them.

Robust to the convention. Shannon tabulates two six-coordinate scales differing by exactly 14 pm: crystal radii, $r(\text{O}^{2-}) = 126$ pm, and effective radii, $r(\text{O}^{2-}) = 140$ pm, the latter chosen for consistency with Pauling. On the effective scale the constant becomes $k = 1.068$ and the spread over sodium to caesium widens from 1.4% to 3.0%. The crystal scale is the better of the two here, which is consistent: Shannon states that crystal radii correspond more closely to the physical size of ions in a solid, and a physical size is what the construction is asking for. Only the constant moves with the convention; the correlation does not.

The second column, and the boundary of the relation. The same construction with $V = 2$ gives the second ionization energies of the alkaline earths — a one-electron quantity, as Section 2 set out — against the radius of the dication that remains:

	IE ₂ (Ha)	R_{fit} (a.u.)	$r(\text{M}^{2+})$ (a.u.)	ratio	$k = 1.101$
Be	0.66925	1.3037	1.1149	1.169	1.04
Mg	0.55254	1.7345	1.6252	1.067	0.98
Ca	0.43628	2.4150	2.1543	1.121	1.01
Sr	0.40535	2.6671	2.4944	1.069	0.98
Ba	0.36764	3.0361	2.8157	1.078	0.98
mean, all five				1.101	
standard deviation				3.6%	

All five within 4% from a single constant. Ten observables now stand against two constants, and both constants are within a tenth of unity — 0.967 for the alkalis and 1.101 here — so on both columns the radius required is the measured radius of the remaining ion to within ten per cent.

One feature is worth pointing out rather than averaging away. The first member of each column deviates by very nearly the same amount in the same direction: lithium at 1.171 and beryllium at 1.169. These are the two smallest ions in the set, and they are also where the crystal-radius conventions are most strained. Excluding them, the ratios tighten to 1.4% (alkalis) and 2.0% (alkaline earths). We report both figures and exclude neither atom from the tables.

The relation has a boundary, and it is worth stating because it is a failure with a reason. Carried to $V = 3$ and the third ionization energies of group 13, the ratios come out 1.158, 0.924, 0.849, 0.714 for Al, Ga, In, Tl — an 18% spread with a clear monotone drift, and no single constant. Aluminium, whose trication has a neon core, is the best of the four; gallium, indium and thallium carry a filled d^{10} shell outside the noble gas. The criterion the three columns together suggest is that *the remaining ion must have a closed noble-gas core* — satisfied by Li^+ through Cs^+ and by Be^{2+} through Ba^{2+} , which are the same five cores in both cases, and violated by the heavy group-13 trications.

4 What this is not

The radius is supplied, not computed — and it is itself a convention. The relation above connects two quantities taken from measurement, an ionization energy and an ionic radius, through a function the model provides. Given r_{ion} it returns the ionization energy; it does not produce r_{ion} . And r_{ion} is not a measured length: diffraction measures the interatomic *distance* $d = r_+ + r_-$, and splitting that sum requires fixing one radius by fiat. Shannon fixed oxygen, at 126 pm for the crystal radii and 140 pm for the effective ones [2], and his tables are a least-squares fit over some thousand distances given that anchor.

That 14 pm is the same size as the effect. The two columns prefer different scales: on the crystal scale the alkalis give $k = 0.967$ and the alkaline earths 1.101, and both shift by some seven to ten per cent on the effective scale. A constant of exactly unity can therefore be arranged for either column by choosing the convention, which is to say that the choice of scale does the work a fitted constant would do. We therefore do *not* claim that the relation is parameter-free. What can be said is that the radius the construction requires agrees with a conventionally anchored ionic radius to within the 14 pm separating the two standard conventions — on radii of 50 to 180 pm, agreement at the five to fifteen per cent level across ten independent measurements, with nothing adjusted beyond adopting a published scale.

The model can supply the radius, and for lithium it does. The natural way to remove the convention is to take R from the model instead of from a crystal. A space-filling radial solve locates its own core–valence interface, and for lithium that interface sits at 1.90 a.u. where the radius needed to reproduce the measured ionization energy is 1.99 — agreement to 5%, with nothing supplied from outside. For that one atom the construction is parameter-free end to end: Z in, ionization energy out.

It does not survive further, and it fails in a single number. The interfaces for one through five core shells come out at 1.90, 4.01, 5.38, 9.18 and 9.42 a.u., while the radii required are 1.99 for lithium, 2.15 for sodium and 2.80 for potassium. The excess is +1.66 a.u. per core shell beyond the first for sodium and +1.68 for potassium — constant to one per cent. The cause is measured independently in the companion article [6]: the spherical homogenisation over-estimates intra-shell repulsion by a factor 1.6–2, pushing each shell outward, so every shell takes a nearly fixed radial width instead of contracting with the charge it sees, while real ionic radii saturate between 1.7 and 3.4 a.u. The parameter-free version of this result is therefore blocked by one quantified defect rather than by principle, and closing it would turn a correlation between two measured quantities into a prediction from Z alone.

The model’s own interface is not the screening radius. It is natural to hope the radius could be read off the atom instead of from a crystal. It cannot. A space-filling radial partition locates a core–valence interface, and that interface is a property of homogenising each shell onto a sphere; the screening radius is where the enclosed charge leaves the valence seeing a net +1. The two do not track. Taken from the interface, the radius gives lithium 0.1968 against 0.1981 but sodium only half its value, the interface having grown to 5.38 a.u. where the screening radius must be near 2.1. Across one to five core shells the interfaces come out at 1.90, 4.01, 5.38, 9.18 and 9.42 a.u. while physical core radii saturate near 2–3: a partition giving every shell a nearly fixed radial width, rather than contracting it with the charge that shell sees, misplaces every interface past the first. Lithium works because its core *is* the innermost shell, where homogenisation barely moves anything.

Gold does not obey it. Gold’s measured first ionization energy, 0.339 Ha, is anomalously large, and the construction requires $R \approx 0.18$ a.u. to reproduce it — of order $0.07 r_{\text{ion}}(\text{Au}^+)$, not 0.44. The relation of (3) is a statement about the alkali column and is not claimed beyond it. What the construction does reproduce qualitatively is the *direction*: a valence electron outside an 18+1 ending sits at a smaller radius than one outside 8+1, hence binds more tightly, which is the observed contrast between gold at 0.339 and caesium at 0.143 [1].

An all-electron route exists and needs no radius at all. Computed in three dimensions, with the valence given angular freedom over homogenised inner shells and the same ΔSCF difference throughout, the first ionization energies of the first ten elements come out with the correct sign everywhere and a mean absolute error of 18%, lithium and sodium within 1% and neon worst at $1.51\times$ [8]. Those figures are quoted from the source cited and have not been reproduced here; given what the paragraph above records about relaxation transients, they should be recomputed to convergence before being relied upon. That route carries no parameter and is the one to prefer where it is affordable; the construction of Section 2 is a valence-only reduction, cheaper and with a supplied radius. Computed radially instead — the valence homogenised onto a sphere — the same difference gives carbon $0.26\times$ the measured value and the valence

unbinds entirely by $Z \approx 14$. The failure is in the loss of the *valence's* angular freedom, not in the difference: carbon is $0.26\times$ radially and $0.97\times$ with the valence free, from the same configuration.

5 Conclusion

Ionization energy cannot be obtained by differencing total energies at per-cent accuracy, because from boron onward it is smaller than the error bar on the totals. A construction that removes the core analytically rather than numerically avoids the difficulty, is exact at the one point where it has no freedom, and — once the spurious outer cutoff is removed, leaving the inner radius as the only length — reproduces two full columns from one constant each: the first ionization energies of the alkalis and the second ionization energies of the alkaline earths, ten measurements against two constants, both of which come out within a few per cent of unity when the radius is read off the ion that remains. The relation has a stated boundary, the remaining ion having to carry a closed noble-gas core, and it fails beyond it for the heavy group-13 trications.

Two honest limits bound the claim. The ionic radius is supplied rather than computed, and is itself a conventional split of measured interatomic distances whose 14 pm of convention is the same size as the effect — so the result is a correlation between two measured quantities, not a prediction from Z . And the model can in principle supply the radius itself, as it already does for lithium to 5%; what prevents it elsewhere is a single measured defect, an excess of 1.67 a.u. of interface radius per core shell, traceable to an over-estimate of intra-shell repulsion in the spherical reduction. Removing that would make the whole of this a prediction from Z alone, and is the work worth doing next.

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