Accurate account of screening in X-ray characteristic radiation. Moseley law and its extension to individual term energies

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December 10, 2025, Talk at the DESY-KIPT Seminar

Contents

Inner-shell atomic spectroscopy at DESY. I

Inner atomic shells play a central role in a variety of processes of X-ray, gamma-ray, and high-energy charged particle inelastic interaction with atomic matter

- X-Ray spectroscopy and imaging
- Electron energy-loss spectroscopy
- X-ray gamma astronomy

The accuracy of such techniques hinges on the intrinsic simplicity of inner shells. In the first approximation, they may be treated as purely hydrogenic, but for practical purposes, a more accurate treatment is mandatory.

Inner-shell atomic spectroscopy at DESY. II

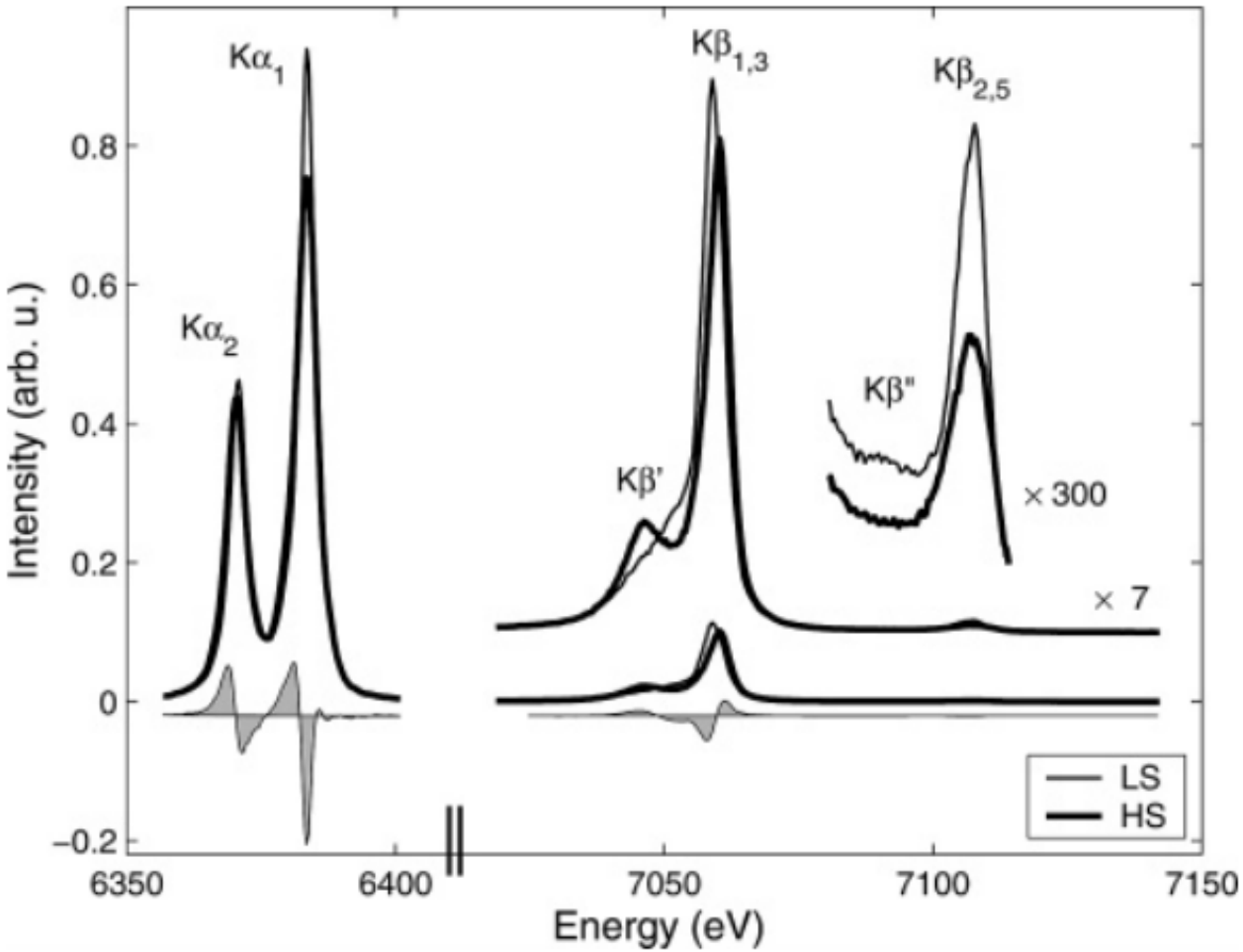


Figure 1: K shell normal x-ray emission spectral lines for a high-spin (HS, thick line) and low-spin (LS, thin line) Fe2+ compound. [1]

Inner-shell atomic spectroscopy at DESY. III

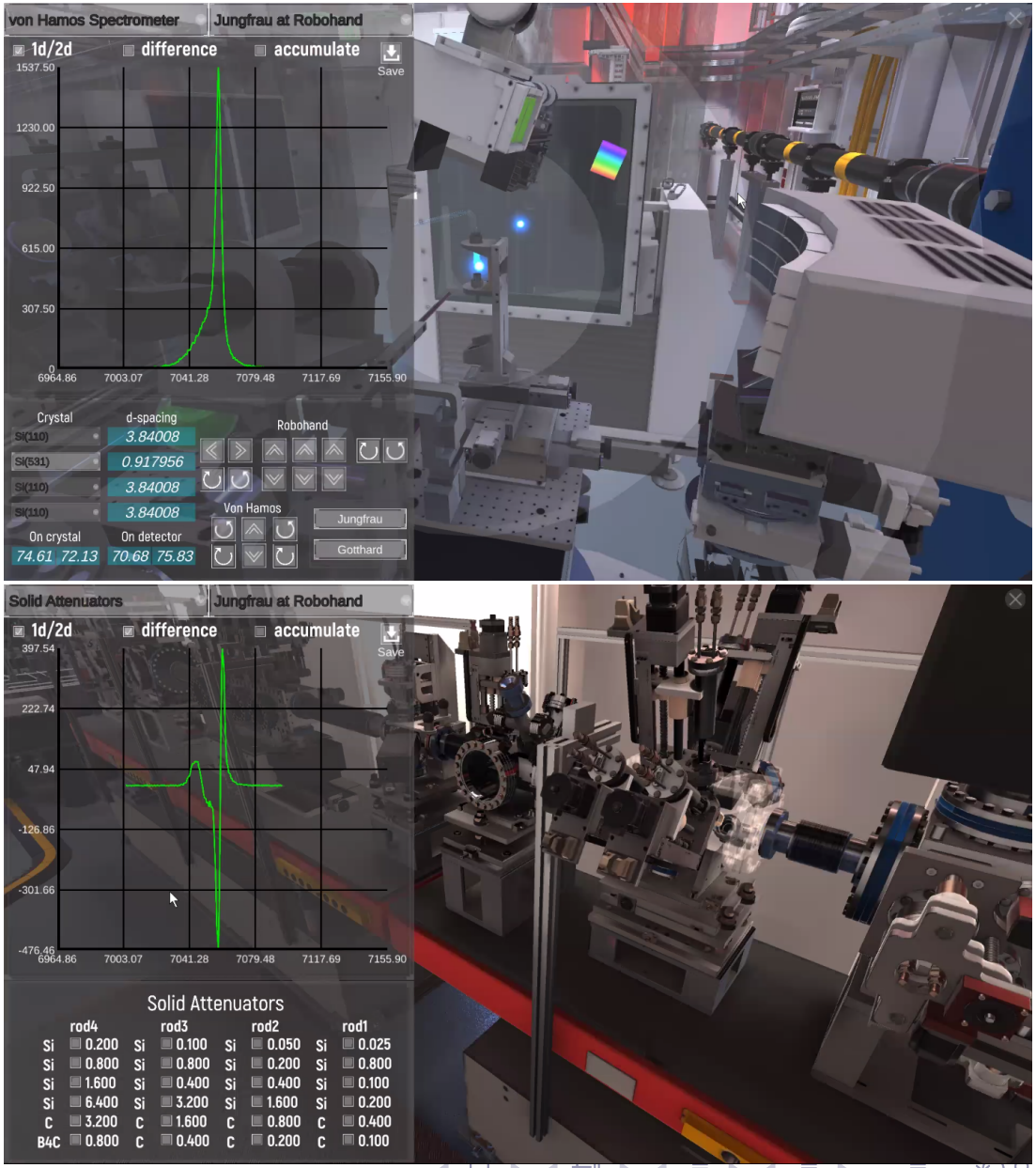
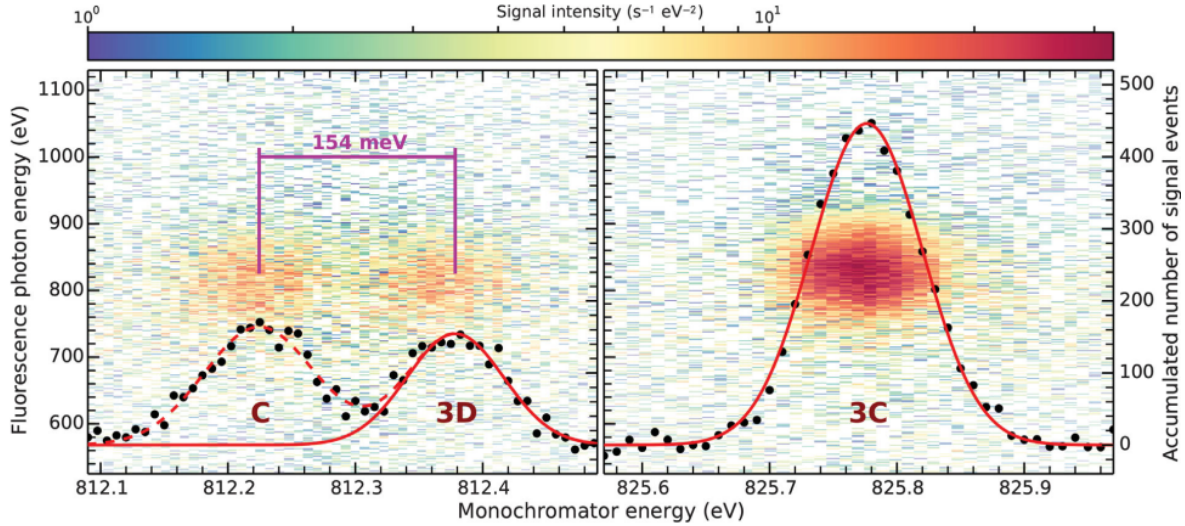
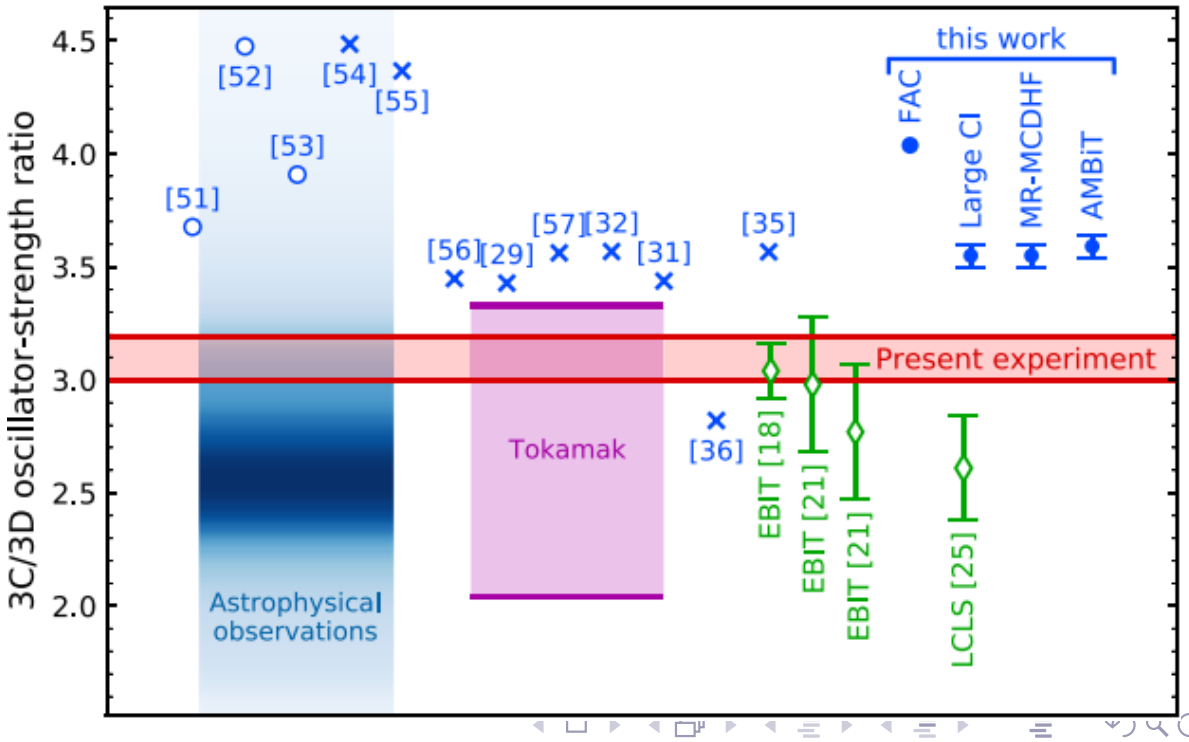


Figure 2: Investigation of excited matter properties at K_β line at EuXFEL. From Virtual Lab presentation by Ch. Bressler [2]

Inner-shell atomic spectroscopy at DESY. IV

Figure 3: Most astrophysical observations and laboratory studies of 2p–3d diagnostic transitions, 3C and 3D, in Fe XVII ions had found oscillator strength ratios $f(3C)/f(3D)$ disagreeing with theory. In [3] these lines were resonantly excited using synchrotron radiation at PETRA III, and a 10 times higher spectral resolution is reached. The final result supports many of the earlier observations, while departing by five sigmas from the newest large-scale ab initio calculations.





Moseley's law for screening effect in ChXR I

Moseley [4] had noticed an apparent systematic deviation from the Rydberg formula. Based on Bohr's planetary atomic model, the only one available at the time, Moseley had interpreted this discrepancy as being due to the nucleus charge screening by the innermost electron(s), and proposed a phenomenological formula

$$E_{n_2 l_2} - E_{n_1 l_1} = \mathrm{Ry}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\left[Z - \sigma_{n_1 l_1, n_2 l_2}(Z)\right]^2, \quad \sigma_{n_1 l_1, n_2 l_2} \sim 1. \quad (1)$$

Here $\mathrm{Ry} = me^4/2\hbar^2$ is the Rydberg constant, $l = 0, 1, 2, \ldots$ is the angular momentum, and $n = l + 1, l + 2, \ldots$ the principal quantum number.
A Z-independent value of σ was compatible with Moseley's experimental data.

Conjecture. Generalizations to individual term energies

From the theoretical point of view, it seems that screening must characterize individual term energies, being different for different electron states.
It was thus conjectured that an analog of (1) exists for them [5, 6, 7, 8]:

$$E_{nl} = -\frac{\mathrm{Ry}}{n^2}\left[Z - \sigma_{nl}(Z)\right]^2 \tag{2}$$

describing the deviation from Bohr's formula

$$E_n^{(0)} = -\frac{\mathrm{Ry}}{n^2}Z^2 \tag{3}$$

for energy levels of an electron in a pure Coulomb field of charge Z.

Problems with the extension

Empirically, however, $\sigma_{nl}(Z)$ in representation (2) did not prove to be constant.

- It does not explain, e.g., why the screening correction σ_{10} for K shell can exceed 2, whereas there is only one K-electron to shield the nucleus Coulomb field from the other K-shell electron.
- Outer electrons contribute to the shift of X-ray energy levels, as well. Indeed, in any shell there are electrons with zero angular momentum, whose quantum mechanical distribution does not vanish at the atomic nucleus.
- At $Z > 50$, the account of relativistic effects will eventually become mandatory, as well.

Amending the extended Moseley law. I

If $Z \gg 1$, typical r in inner shells are small, allowing one to expand

$$V(r) = -\frac{Z}{r} g(r) \underset{r\to 0}{\simeq} -\frac{Z}{r} - Z g'(0). \tag{4}$$

The explicit dependence of $g'(0)$ on Z may be found in the Thomas-Fermi approximation:

$$g'(0) = -\frac{1.59}{a_{TF}(Z)}, \qquad a_{TF} = 0.885\, Z^{-1/3} a_B. \tag{5}$$

However, since the energy correction term

$$E_{nl}^{(1)\mathrm{scr}} = -Z g'(0) = 1.80 Z^{4/3} \tag{6}$$

is independent of the electron quantum numbers, it will not alter the Rydberg formula for the frequency $E_{n_2 l_2} - E_{n_1 l_1}$ of transitions between different inner shells, at variance with the Moseley's observation.
It also contradicts, e.g., the level splitting due to screening in the L shell.
The leading-term expansion (6) thus appears to be insufficient.

Amending the extended Moseley law. II

To reach beyond (6), it was argued in [9] that the next-order correction to the energy of an electron in an n-th shell must be of the order of the Coulomb interaction between inner-shell electrons. The sign of this interaction energy is positive. Instead of (2) it implies the Z dependence of individual energy terms to be

$$E_{nl} \simeq E_n^{(0)} - Zg'(0) \oplus \frac{Z}{n^2}\delta_{nl}, \tag{7a}$$

$$\approx -Zg'(0) - \frac{1}{2n^2}(Z - \delta_{nl})^2, \qquad \delta_{nl} > 0. \tag{7b}$$

For energy differences between inner atomic shells it leads back to the Moseley law (1). However, it does not guarantee σ to be positive, and is at variance with table data on shell ionization energies.

To amend the reasoning of [9], we need to take into account the similar r-dependent part of the electron-nucleus interaction, which must be of the same order or even dominant due to its coherence. But if accounted for, such a contribution can change sign of the screening correction δ_{nl}.

Our approach. Perturbative account of screening. I

Working in atomic units, we describe inner shells by a single-electron wave function satisfying the radial Schrödinger equation

$$\frac{1}{r}\frac{d^2}{dr^2}rR_{nl}(r) + 2\left[E_{nl} + \frac{Z}{r}g(r) - \frac{l(l+1)}{r^2}\right]R_{nl}(r) = 0 \tag{8}$$

and normalization condition

$$\int_0^\infty drr^2 R_{nl}^2(r) = 1. \tag{9}$$

Our approach. Perturbative account of screening. II

The radii of inner atomic shells are $\sim Z^{-1}$. On the other hand, the radius of a many-electron atom $a_{TF} \sim Z^{-1/3}$ is many times greater if $Z \gg 1$. Hence, in the region where the wave function of the inner atomic shell is concentrated, the deviation of the screening function $g(r)$ from unity is small. The influence of this deviation can therefore be taken into account by means of perturbation theory.

$$E_{nl} \approx E_n^{(0)} + E_{nl}^{(1)}, \tag{10}$$

can be evaluated using the well-known formula [9] of time-independent perturbation theory as the average of the perturbation operator over the unperturbed state:

$$E_{nl}^{(1)\mathrm{scr}} = \langle \psi_0 | Z \frac{1 - g(r)}{r} | \psi_0 \rangle = Z \int_0^\infty dr r \left[R_{nl}^{(0)}(r) \right]^2 [1 - g(r)]. \tag{11}$$

Given that $g'(0)$ is properly described by the TF approximation, it may be self-consistent as well to apply it to the entire $g(r)$.

TF power series. I

Moreover, one may hope to use the power expansion of the TF screening function beyond the linear term (6), to describe the nonuniformity of the screening correction to the Coulomb potential:

$$g(r) \approx \phi_{TF}\left(\frac{r}{a_{TF}(Z)}\right) \underset{r\to 0}{\simeq} 1 - 1.59\frac{r}{a_{TF}(Z)} + \frac{4}{3}\left(\frac{r}{a_{TF}(Z)}\right)^{3/2}. \quad (12)$$

If this expansion is employed in (11), the integral is expressed as

$$E_{nl}^{(1)\mathrm{scr}} = 1.80Z^{4/3}\ominus\frac{32Z}{9\pi}\left\langle\sqrt{2Zr}\right\rangle_{nl}^{(0)}. \quad (13)$$

The average of $\sqrt{2Zr}$ over a hydrogenic state is of the order of $1.5n$, and is evaluated by the generic formula

$$\langle f(r)\rangle_{nl}^{(0)} = \int_0^\infty dr r^2\left[R_{nl}^{(0)}(r)\right]^2 f(r).$$

TF power series. II

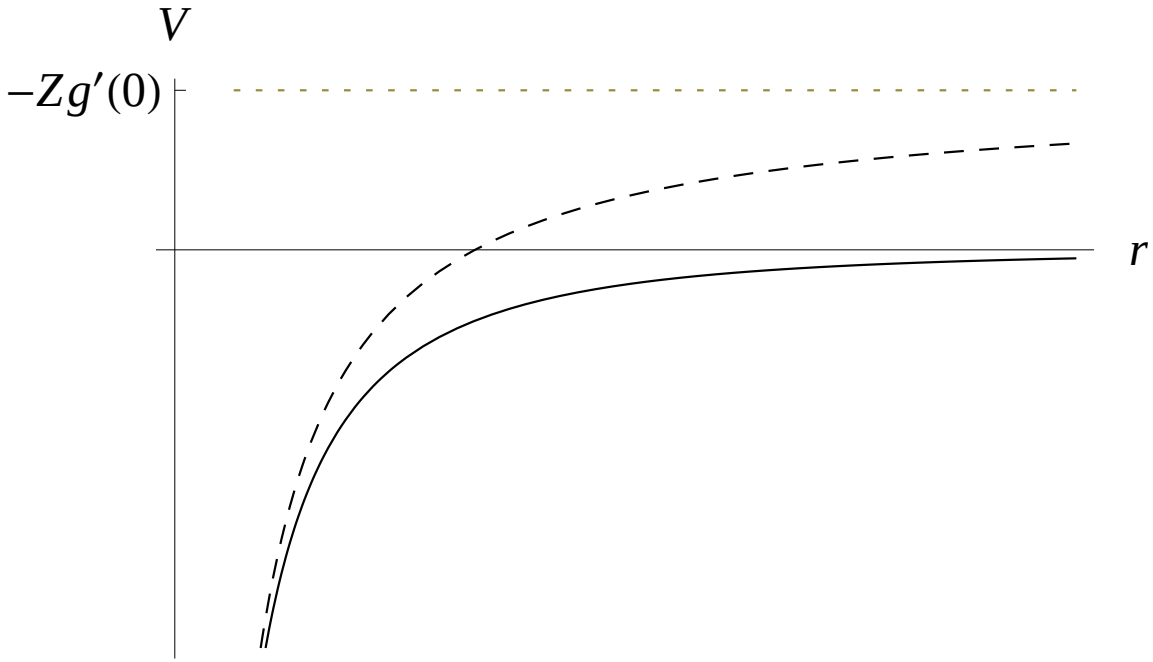


Figure 4: Comparison of the screened atomic potential (solid curve) and its low-r approximation (4) (dashed curve). The exact result is everywhere lower, whence the correction to (6) must be negative.

TF power series. III

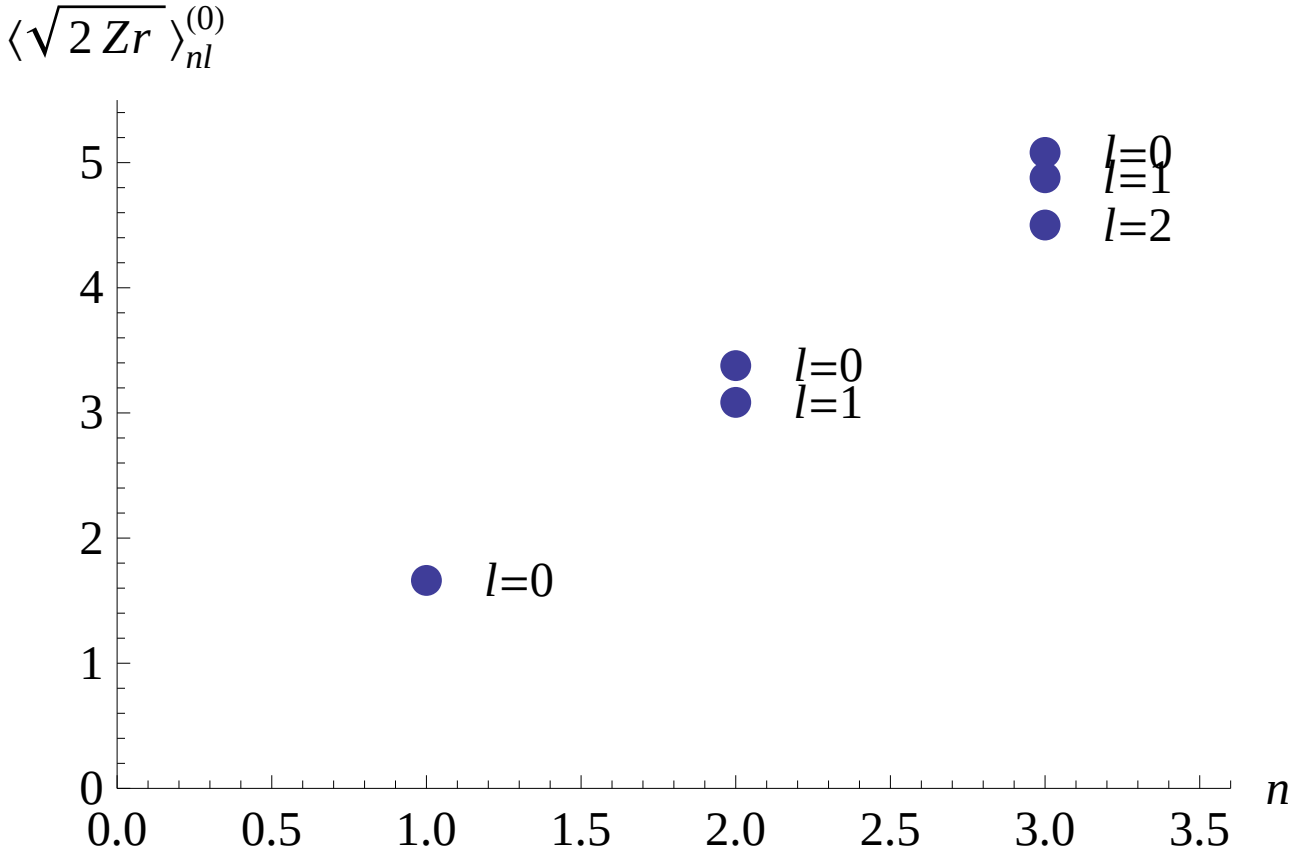


Figure 5: Mean values of $\sqrt{2Zr}$ over hydrogenic wave functions with quantum numbers n, l. For a given n, the value of l increases downwards.

TF power series. IV

The explicit microscopic expression for the screening constant then follows in form

$$\sigma_{n_1 l_1, n_2 l_2} = \frac{32}{9\pi} \frac{\left\langle \sqrt{2Zr} \right\rangle^{(0)}_{n_2 l_2} - \left\langle \sqrt{2Zr} \right\rangle^{(0)}_{n_1 l_1}}{n_1^{-2} - n_2^{-2}} > 0. \tag{14}$$

Its positivity holds despite the opposite signs of the last terms in (7a) and (13).
It owes to the fact that the absolute value of the Bohr energy (3) decreases with n, while the magnitude of the screening correction determined by $\left\langle \sqrt{Zr} \right\rangle^{(0)}_{nl} \propto n$ increases with n.

Relativistic correction

The most significant correction to the Bohr energy apart from the screening correction is due to the relativistic character of the inner electron motion in a strong field near the atomic nucleus. Treating this correction as a perturbation, too,

$$E_{nlj}^{(1)} = E_{nl}^{(1)\mathrm{scr}} + E_{nj}^{(1)\mathrm{rel}}. \tag{15}$$

we may employ the well-known expression for the fine-structure energy [**?**]:

$$E_{nj}^{(1)\mathrm{rel}} = E_{n}^{(0)} \frac{(Z\alpha)^2}{n} \left(\frac{1}{j+1/2} - \frac{3}{4n} \right), \tag{16}$$

with $j = l \pm 1/2$ the total angular momentum and $\alpha \approx 1/137$ the fine structure constant.

Numerical results. I

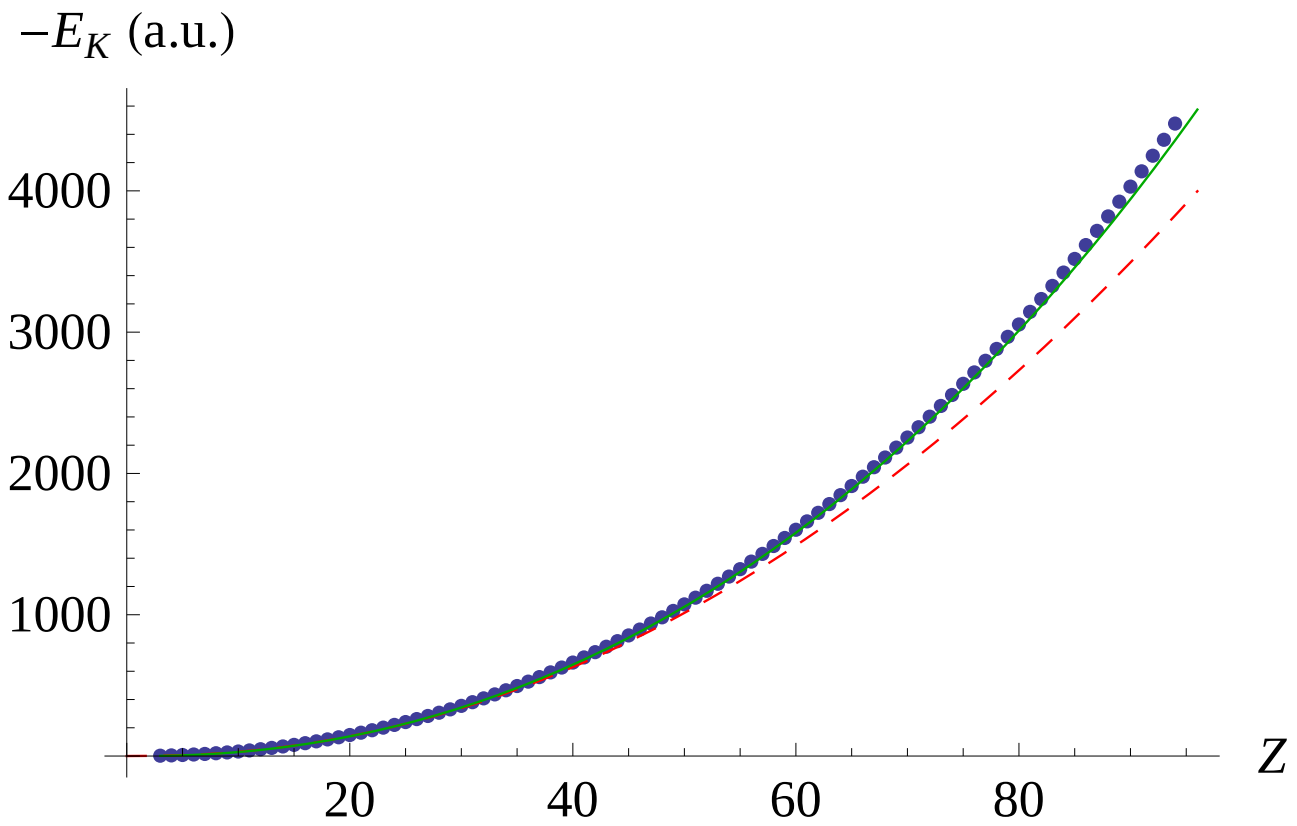


Figure 6: K-shell electron binding energy vs the atomic number Z. Red dashed curve, pure screening correction (11), indistinguishable from (13). Green solid curve, the screening plus relativistic correction (15), (11), (16). Points – table data [10].

Numerical results. II

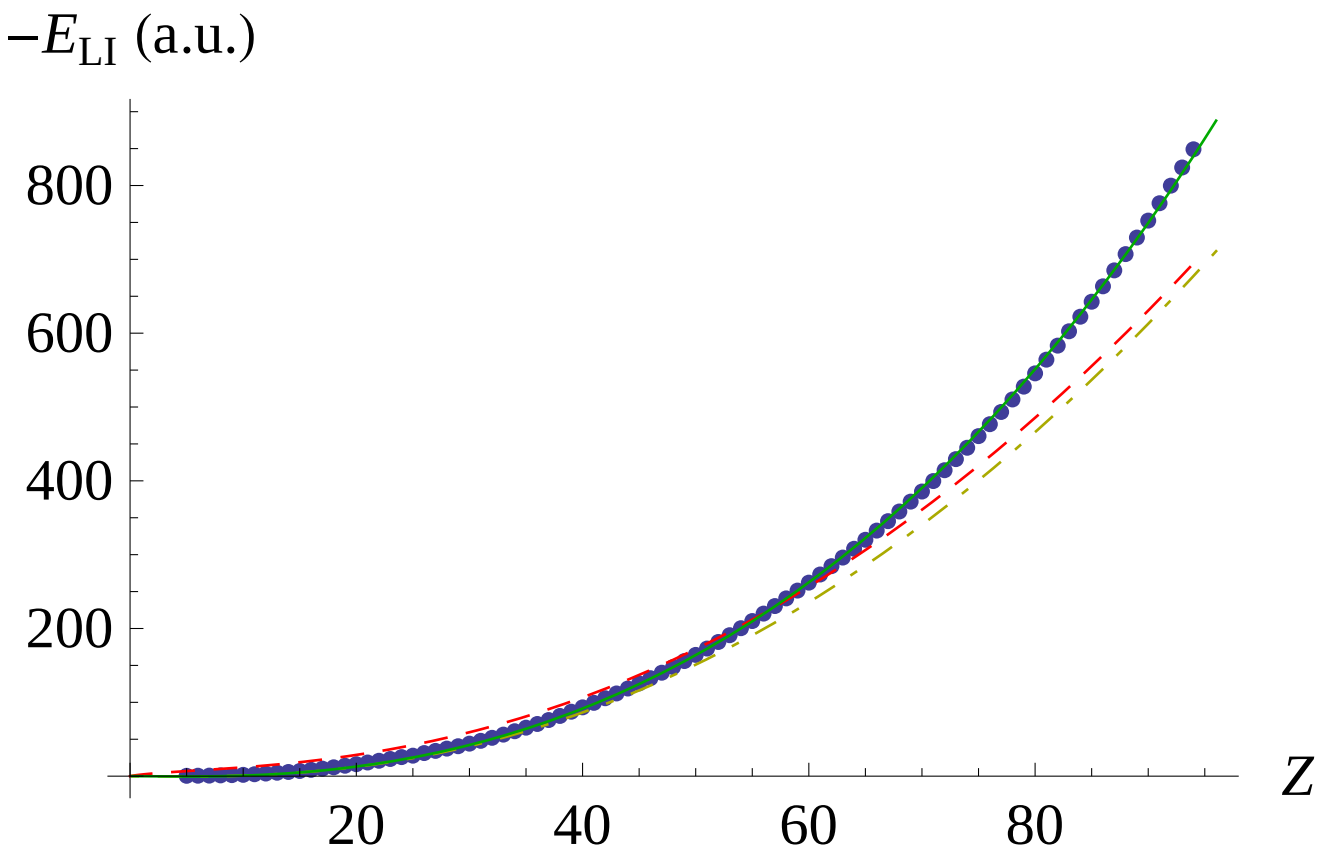


Figure 7: L1-shell electron binding energy vs the atomic number Z. Yellow dot-dashed curve, pure screening correction (11). Red dashed curve, its power-law approximation (13). Green solid curve, the screening plus relativistic correction (15), (11), (16). Points – table data [10].

Numerical results. III

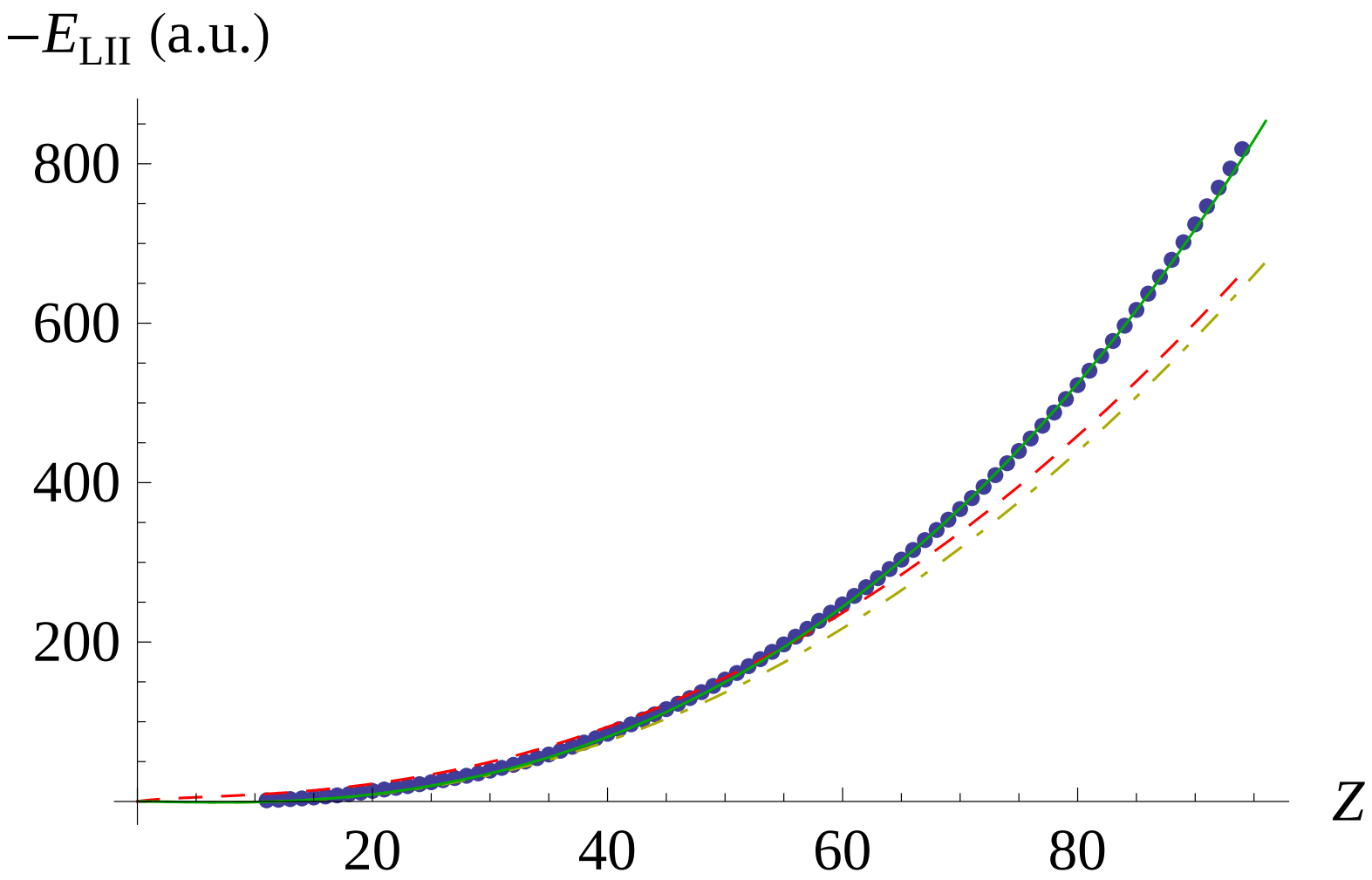


Figure 8: The same as Fig. 7, for L2 shell.

Numerical results. IV

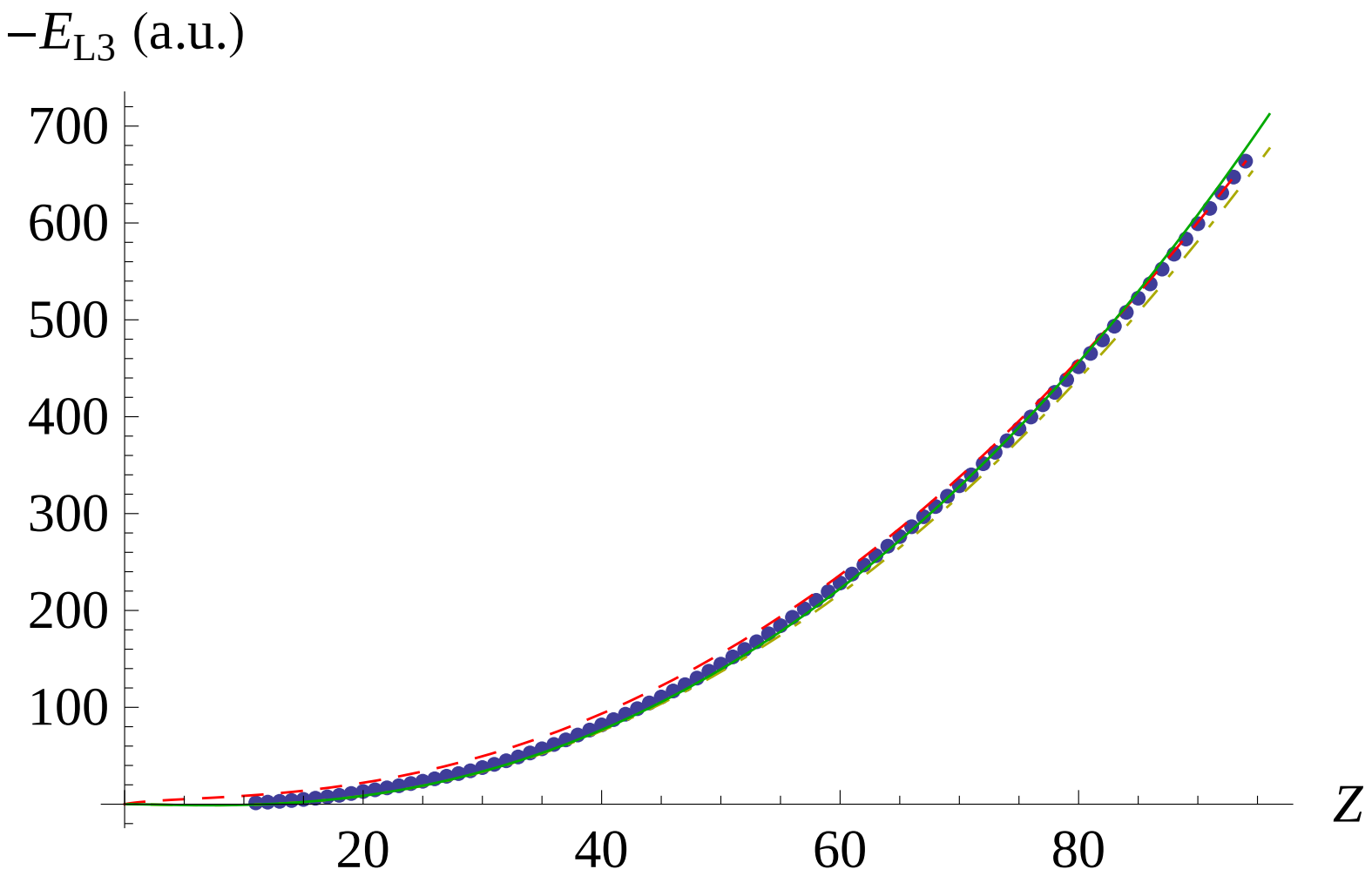


Figure 9: The same as Fig. 7, for L3 shell.

Conclusions

Moseley law proves to be compatible with the description of inner shell screening as furnished by all the atomic electrons, which is well tractable even by the Thomas-Fermi approximation.
This resolves some contradictions present in approaches attributing the screening to electrons comprising the inner shell itself.
In particular, the sign of δ_{nl} in representation (7b) turns out to be negative, not being explainable by the reduction of the effective Z.
The perturbative treatment of the screening correction combined with the Thomas-Fermi approximation already lends a good agreement of the individual electron term energies with the table data, provided the relativistic correction is taken into account, as well.
Presenting the electron term energy, in the spirit of the Moseley law, as a low-order polynomial in Z [Eqs. (10), (3), (13)], however, is found to be numerically accurate only for the K shell.
For L shell, the spatial scales $a_{TF} \sim Z^{-1/3}$ for the Thomas-Fermi screening and n^2/Z for the hydrogenic shell radii turn out to be commensurate for $Z < 100$. For this reason, Z dependence of the integral (11) does not reduce to a power law.

Future plans

Apart from atomic electron energies, many applications require the knowledge of the electron wave functions. For inner atomic shells, the presence of two different spatial scales creates premises for efficient evaluation of the electron wave functions, as well.
The corresponding results [11] are to be reported elsewhere.

List of experiments on LPM suppression

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