

# Data-based predictions of line strengths in alkali-metal-like isoelectronic sequences

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The empirically observed isoelectronic linearization of alkali-metal-like line strengths  $Z^2S = A + B/(Z - C)$  is examined for the Li, Na, Cu, and Ag sequences. It is found that small deviations from this linearity observed at high  $Z$  can be removed by use of a correction factor obtained from the relativistic formulation of the hydrogenlike line strength. With this correction, low- $Z$  data can be linearly interpolated to the nonrelativistic hydrogenic value in the high- $Z$  limit. The linearization is tested in the data-rich Li, Na, and Cu sequences and is utilized to make precise predictions for the Ag sequence on the basis of a small number of accurate measurements.

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## I. INTRODUCTION

It has been established experimentally [1-5] that atomic transition line strengths in alkali-metal-like and alkaline-earth-metal-like isoelectronic sequences are well represented for moderate stages of ionization by the empirical relationship

$$Z^2S \cong A + B/(Z - C), \quad (1)$$

where  $S$  is the line strength,  $Z$  is the nuclear charge, and  $A$ ,  $B$ , and  $C$  are empirical fitting parameters. Examples of this exposition for the lowest  $s$ - $p$  resonance transitions in the Li, Na, and Cu sequences are displayed in Fig. 1. This linearizing exposition is of utilitarian value for the precise interpolation and extrapolation of measured data, irrespective of its origin and implications in fundamental theory. However, the existence of these clear linearities in measured data, which are not always exhibited by theoretical calculations, also raises intriguing theoretical questions. Recent measurements in very highly ionized members of these sequences have indicated a slight downward deviation from the linear trend when the stage of ionization exceeds approximately 40. We have undertaken a study of this high- $Z$  behavior and have found that, through a slight modification to Eq. (1), the linearity can be restored, permitting precision data-based predictions for all members of the alkali-metal-like isoelectronic sequences.

## II. COMPUTATIONAL FORMALISM

For purposes of this formulation, the line strength will be considered as an experimentally determined quantity. It can be deduced from experimental measurements of the transition probability rate  $A_{ul}$  and the transition wavelength  $\lambda_{ul}$  for a transition from an upper level  $u$  to a lower level  $l$  using

$$S = [\lambda_{ul}(\text{\AA})/1265.38]^3 (2J_u + 1) A_{ul} (ns^{-1}), \quad (2)$$

where  $J_u$  is the total angular momentum of the upper level.

The deviation from the linear representation by Eq. (1) at very high stages of ionization could arise from a number of alternative mechanisms. One possible mechanism could involve the breakdown of the  $Z$  independence of the screening parameter  $C$  due to the entry into a new and altered regime of interactions involving, e.g., core penetration, core-electron correlations, quantum electrodynamic interactions, or finite nuclear size effects. This mechanism can be empirically tested by replacing  $C$  with a continuous iterative screening approximation, as has been proposed by Froese Fischer [6]. Another (less complicated) possible mechanism could involve relativistic (and possibly retardation and quantum electrodynamic) modifications to the active electron alone, with a core that is still characterized by a  $Z$ -independent screening constant  $C$ . This mechanism can be tested by correcting the line strength for the relativistic variations with  $Z$  of the corresponding hydrogenlike value, as has been suggested by Younger and Weiss [7]. We have empirically investigated these two phenomenological models and have concluded that the experimental data can be linearized through corrections that involve only the orbital electron and thereby preserve the constancy of the screening parametrization.

As can be seen from Figs. 1(a)-1(c), the linear trend established from data with low to medium  $Z$  intersects the  $1/(Z - C) = 0$  axis (corresponding to the high- $Z$  limit) almost exactly at the nonrelativistic hydrogenic values  $S_H(1)$  (designated by X on these plots), which are given, for an  $ns - np$  transition, by [8]

$$S_H(1) = \frac{3}{4} n^2 (n^2 - 1) (2J_u + 1). \quad (3)$$

The nonrelativistic  $Z$  dependence for the hydrogenlike isoelectronic sequence is given simply by  $Z^2 S_H(Z) = S_H(1)$ , but the corresponding relativistic value  $S_H^R(Z)$  is of the form

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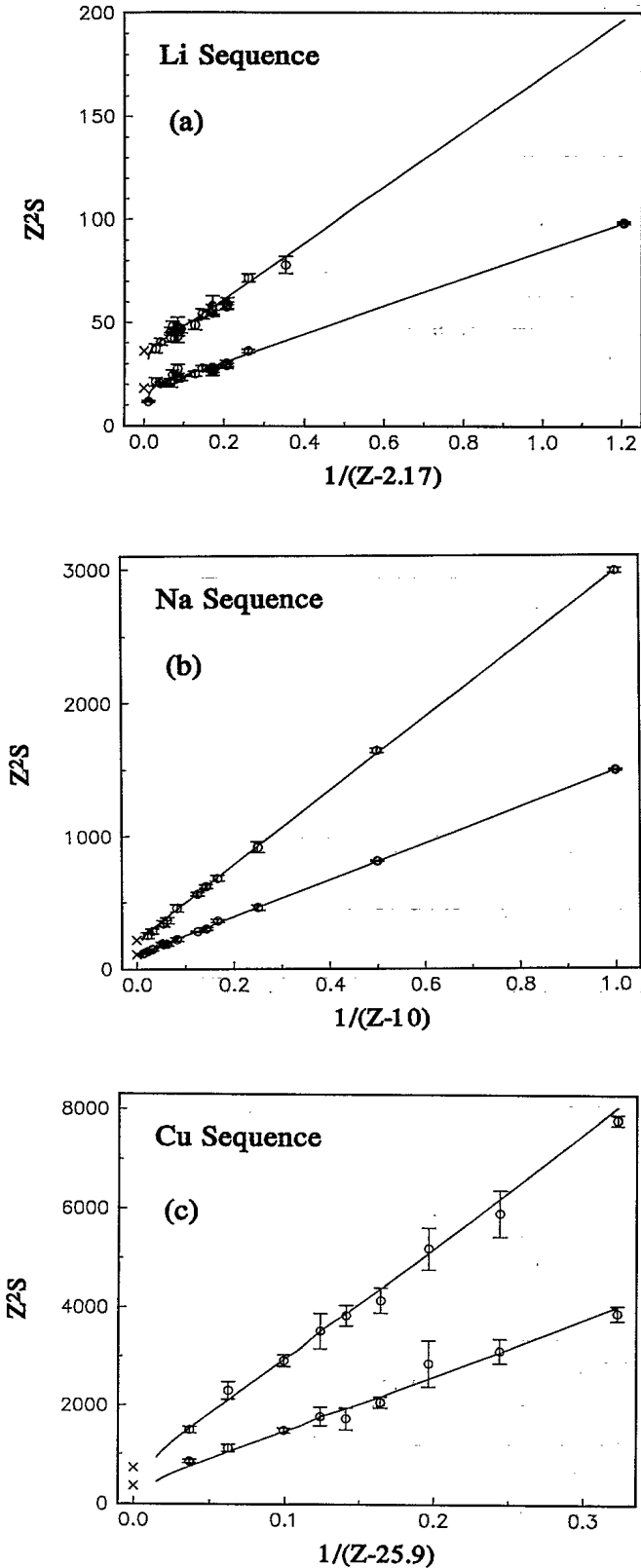


FIG. 1. Plots of the nuclear-charge-scaled line strength vs the reciprocal screened central charge for the  $ns-np$  transitions in the (a) Li ( $n=2$ ), (b) Na ( $n=3$ ), and (c) Cu ( $n=4$ ) isoelectronic sequences. Experimental measurements are denoted by O, the solid curves trace semiempirical calculations using the CAHS method, and the hydrogenic values are designated by X.

$$Z^2 S_H^R(Z) = S_H(1) \left[ 1 - \sum_i a_i (\alpha Z)^{2i} \right]. \quad (4)$$

We have calculated the dipole line strengths as a function of  $Z$  using hydrogenlike Dirac wave functions, employing the symbolic algebra computational package MAPLE [9]. In this calculation we have neglected retardation effects, assuming no variation in the electromagnetic field over the dimensions of the atom. Quantum electrodynamic effects were also neglected. For the  $ns_{1/2}-np_{1/2}$  transitions, the result can be written in a particularly simple form (owing to the Dirac degeneracy of levels of opposite parity having the same values of  $n$  and  $J$ ). This form, together with an expansion demonstrating that the values of  $a_i$  for this case are rational fractions, is presented in the Appendix below. Numerical values for  $S_H(1)$  and  $a_i$  are presented in Table I. For the  $ns_{1/2}-np_{3/2}$  transition, the  $a_i$  coefficients for  $i > 1$  are irrational, involving the Riemann  $\zeta$  function and factors of  $\pi$ , and are presented in decimal form. For the  $2s-2p$  and  $3s-3p$  cases, our calculations agree with earlier numerical calculations by Younger and Weiss [7], which used the same approximations.

The low- $Z$  data in Figs. 1(a)–1(c) exhibit linear trends that extrapolate almost exactly to the hydrogenic values  $S_H(1)$  in the high- $Z$  limit. This suggests that a parametrization by the relativistic hydrogenic value in Eq. (4) might be useful in characterizing the observed behavior of alkali-metal-like systems. We have tested the effect of these relativistic corrections by forming the quantity

$$\frac{Z^2 S}{1 - \sum_i a_i [\alpha(Z-C)]^{2i}} \cong S_H(1) \left[ A' + \frac{B'}{Z-C} \right]. \quad (5)$$

The forms of Eqs. (1) and (5) raise interesting questions concerning the phenomenological parametrization of charge screening. Why in Eq. (1) is the line strength scaled by the square of the fully stripped nuclear charge  $Z$ , whereas its deviation from isoelectronic constancy is scaled as the reciprocal of the nearly fully screened core charge  $(Z-C)$ ? (Note that the fitted values  $C = 2.17$ ,  $10.0$ , and  $25.9$  for the Li, Na, and Cu sequences correspond to core electron numbers 2, 10, and 28, respectively.) Similarly, why in Eq. (5) have we chosen to use  $(Z-C)$  rather than  $Z$  in the relativistic correction factor? The utilitarian answer to both of these questions is that this formulation provides a higher degree of linearity in the exposition than any of the other choices considered. Plausibility arguments can also be raised that the dipole transition moment scales as the basic Hartree coordinate of the atom  $r/2Za_0$ . However, the corrections to the constancy of this quantity in the Hartree scale arise because of the scaling of the orbital electron wave function, which arises from monopole electrostatic interactions.

### III. DATA SOURCES

Experimental lifetime data were drawn from Refs. [10–27] for the Li sequence, from Refs. [10,28–37] for the Na

TABLE I. Constants for relativistic hydrogenlike line strengths.

Transition	$S_H(1)$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$
$2s_{1/2}-2p_{1/2}$	18	5/6	-1/48	1/96	7/768	11/1536
$2s_{1/2}-2p_{3/2}$	36	1/3	0.110187	0.059476	0.037032	0.024925
$3s_{1/2}-3p_{1/2}$	108	7/12	5/144	7/288	37/2304	53/4608
$3s_{1/2}-3p_{3/2}$	216	19/72	0.139267	0.082219	0.050840	0.033291
$4s_{1/2}-4p_{1/2}$	360	9/20	3/64	17/640	87/5120	123/10240
$4s_{1/2}-4p_{3/2}$	720	103/480	0.147237	0.093466	0.058853	0.038459
$5s_{1/2}-5p_{1/2}$	900	11/30	29/600	31/1200	157/9600	221/19200
$5s_{1/2}-5p_{3/2}$	1800	9/50	0.150012	0.100133	0.064068	0.041970

sequence, from Refs. [38–48] for the Cu sequence, and from Refs. [49–57] for the Ag sequence. In selecting these data, preference was given to measurements that eliminated the effects of cascade repopulation, either through laser selective excitation methods or through correlated decay curve analysis [58].

For the Li, Na, and Cu sequences, our comparisons with experimental data have been complemented by similar comparisons with published results obtained by the semiempirical Coulomb approximation with Hartree-Slater core (CAHS) method [59–61]. The CAHS method does not test *ab initio* theory, but instead uses measured energy level and core polarization data to test whether those wave functions that best describe energy levels also describe transition probabilities. These CAHS calculations have been found to accurately match the experimental data base for all but the highest values of  $Z$  and they partially incorporate relativistic effects by virtue of the use of experimental energy levels as inputs. However, its basis in the Schrödinger equation requires some caution in its application to very high  $Z$ .

#### IV. RESULTS

The results of the application of the relativistic corrections to the Li, Na, and Cu sequences are shown for the high- $Z$  regions in Figs. 2, 3, and 4, respectively. In each of these figures the upper plot [labeled (a)] is reduced using Eq. (1) and the lower plot [labeled (b)] is reduced using Eq. (5). The relativistic corrections do not significantly alter the ordinate at moderate  $Z$ , but, as can be seen from Figs. 2(b), 3(b), and 4(b), they nearly eliminate the deviation from linearity that occurs at  $(Z - C) \cong 40$  in Figs. 2(a), 3(a), and 4(a).

The large amount of lifetime data for highly charged ions in the Li, Na, and Cu sequences confirms the existence of this linearizing relationship and provides some confidence that the method can be applied to other sequences for which a smaller data base of lifetimes exist. An example of such an application to the  $5s-5p$  transitions in the Ag sequence is shown in Fig. 5. (For the higher ionization stages of this sequence the plunging  $4f$  becomes the ground configuration and the  $5s-5p$  are no longer resonance transitions.) In the cases of Ag I [49] and Cd II [50], high-precision lifetime measurement results utilizing selective laser excitation are available. Assuming that Eq. (5) is valid for this system, the fits

indicated by the solid lines in Fig. 5 were made by adjusting the value of  $C$  (common to both the  $1/2-1/2$  and  $1/2-3/2$  transitions) to optimize the linearity in this exposition of the Ag I and Cd II points and the hydrogenic values  $S_H(1)$  at the  $1/(Z - C) = 0$  asymptotic limit. Based on this assumption, all other values for  $Z^2S$  for this sequence can be obtained by interpolation.

Values obtained for the parameters  $A'$  and  $B'$  through least-squares adjustment to the measured data and the CAHS calculations for the Li, Na, Cu, and Ag sequences

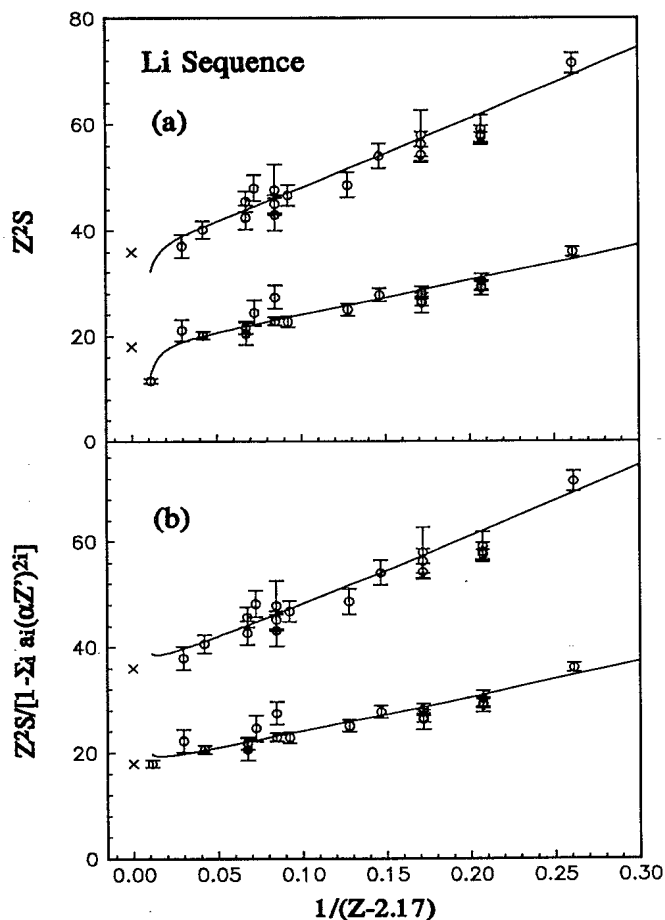


FIG. 2. Comparison of the high- $Z$  region of Fig. 1(a) (the Li sequence) (a) without and (b) with the relativistic corrections. Experimental measurements are denoted by O, the solid curves trace semiempirical calculations using the CAHS method, and the hydrogenic values are designated by X.

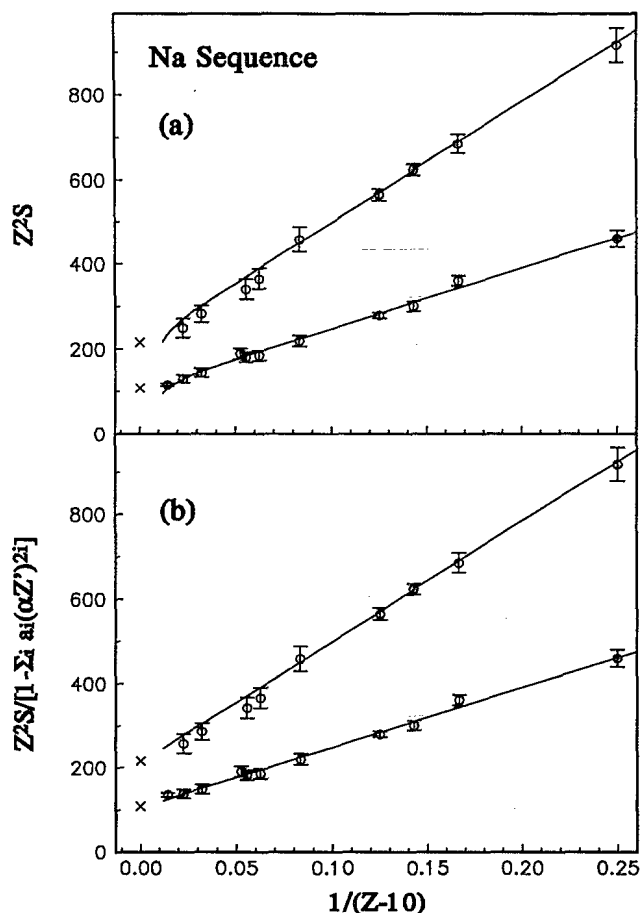


FIG. 3. Comparison of the high- $Z$  region of Fig. 1(b) (the Na sequence) (a) without and (b) with the relativistic corrections. Experimental measurements are denoted by O, the solid curves trace semiempirical calculations using the CAHS method, and the hydrogenic values are designated by X.

are given in Table II. Predictions for all four sequences can either be read directly off Figs. 1–5 or computed precisely from Eqs. (3) and (5) and the values presented in Table II. The accuracy of these predictions could be further tested by a few selected lifetime measurements at very high  $Z$ . Application of these techniques to other transitions and other similar sequences requires only the existence of a sufficiently comprehensive and reliable data base of lifetime measurements.

TABLE II. Fitted parameters.

Sequence	Transition	$A'$	$B'$	$C$
Li	$2s_{1/2}-2p_{1/2}$	1.008	3.65	2.17
	$2s_{1/2}-2p_{3/2}$	1.003	3.660	
Na	$3s_{1/2}-3p_{1/2}$	0.997	12.91	10.0
	$3s_{1/2}-3p_{3/2}$	0.997	12.78	
Cu	$4s_{1/2}-4p_{1/2}$	0.943	31.53	25.9
	$4s_{1/2}-4p_{3/2}$	0.952	31.60	
Ag	$5s_{1/2}-5p_{1/2}$	1.062	27.01	44.7
	$5s_{1/2}-5p_{3/2}$	0.985	26.63	

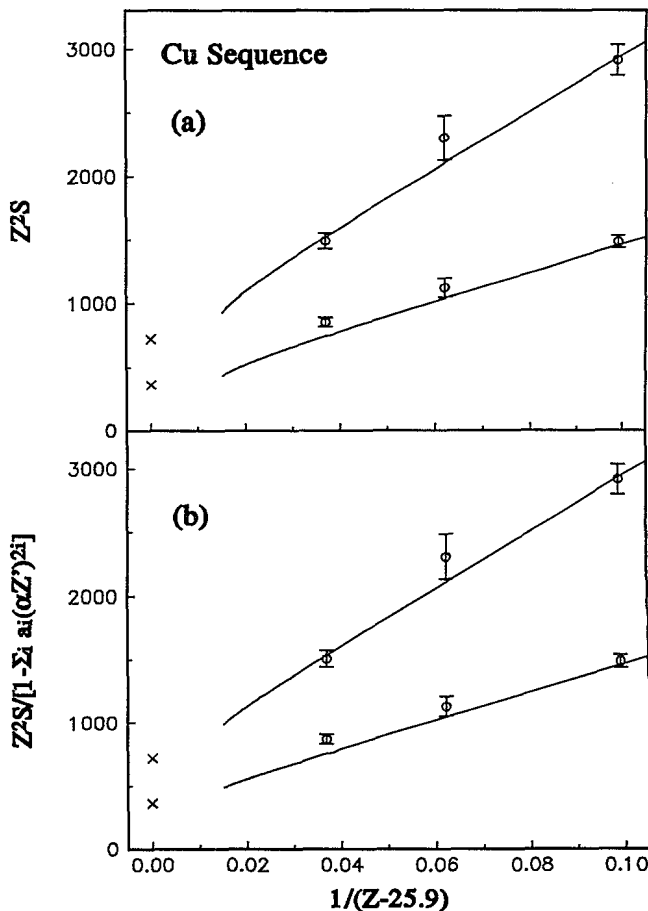


FIG. 4. Comparison of the high- $Z$  region of Fig. 1(c) (the Cu sequence) (a) without and (b) with the relativistic corrections. Experimental measurements are denoted by O, the solid curves trace semiempirical calculations using the CAHS method, and the hydrogenic values are designated by X.

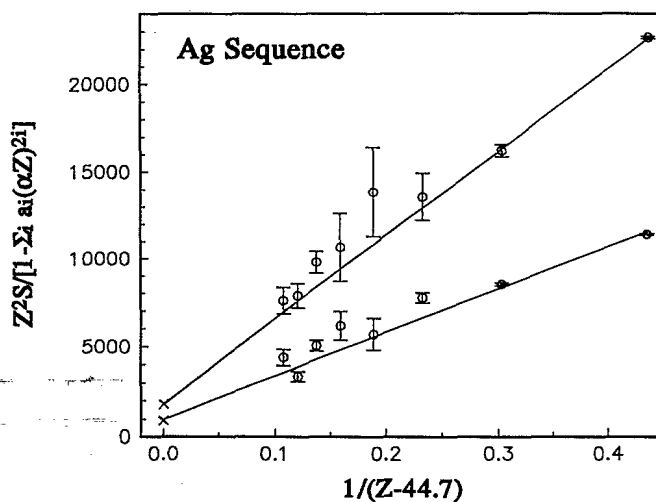


FIG. 5. Plot of the nuclear-charge-scaled line strength vs the reciprocal screened central charge for the  $5s-5p$  transitions in the Ag isoelectronic sequence. The solid lines represent a least-squares adjustment of Eq. (5) to the Ag I and Cd II data and the  $S_H(1)$  high- $Z$  limit.

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## APPENDIX: THE EXPLICIT HYDROGENIC EXPRESSION

In terms of the quantities

$$\gamma \equiv \sqrt{1 - (\alpha Z)^2},$$

$$N \equiv \sqrt{n^2 + 2(n-1)(\gamma-1)},$$

$$\varepsilon \equiv \left[ 1 + \left( \frac{\alpha Z}{n-1+\gamma} \right)^2 \right]^{-1/2},$$

the scaled hydrogenlike line strength for the  $1/2-1/2$  transition can be written, in atomic units, as

$$Z^2 S(ns_{\frac{1}{2}} - np_{\frac{1}{2}}) = \frac{(N^2 - 1)[N^2 + (n-1)\varepsilon N + n(n-2)]^2}{6(n-1)^2}.$$

This can be expanded

$$Z^2 S(ns_{\frac{1}{2}} - np_{\frac{1}{2}}) \cong \frac{3}{2} n^2 (n^2 - 1) \left[ 1 - \frac{1}{n(n+1)} \left( (2n+1)(\alpha Z)^2 + \frac{2n^2 - 4n - 1}{4n} (\alpha Z)^4 + \frac{2n^2 - 4n + 1}{8n} (\alpha Z)^6 + \frac{10n^2 - 20n + 7}{64n} (\alpha Z)^8 + \dots \right) \right].$$

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