Fine structure and analytical quantum-defect wave functions

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We investigate the domain of validity of previously proposed analytical wave functions for atomic quantum-defect theory. This is done by considering the fine-structure splitting of alkali-metal and singly ionized alkaline-earth atoms. The Landé formula is found to be naturally incorporated. A supersymmetric-type integer is necessary for finite results. Calculated splittings correctly reproduce the principal features of experimental values for alkali-like atoms.

I. INTRODUCTION

Departures from Coulomb behavior in the spectra of alkali-metal atoms are dominated by the lowering of energy levels due to the penetration by the valence electron of the core of closed shells surrounding the nucleus. Rydberg presented[1] an empirical formula for the energy levels that incorporates these effects. As a function of the principal quantum number n and the orbital angular momentum l, the energy $E(n,l)$ is

$$E(n,l)=-\frac{E_0}{n^{*2}} . \tag{1.1}$$

Here, E_0 is a constant with the dimensions of energy and n^* is given by

$$n^*=n-\delta(l) , \tag{1.2}$$

where the quantum defect $\delta(l)$ is approximately constant for fixed l. Rydberg's formula correctly describes the gross features of alkali-metal-atom spectra.[2]

In the limit of vanishing electron-electron interactions, the valence spectra of different atoms and ions can be interrelated using supersymmetry.[3,4] Inspired by this, we have previously presented[5] an effective radial equation for a valence electron that is exactly solvable and that has the Rydberg series as eigenvalues. The corresponding analytical eigenfunctions were used to determine transition probabilities for alkali-metal atoms. These were found to be in good agreement with experiment.[5] The eigenfunctions have also been used as trial wave functions for detailed numerical calculations.[6]

Now, transition probabilities involve expectation values of radial distances r^1. The wave functions themselves normalize to r^0. The eigenenergies essentially involve expectation values of r^{-1} and r^{-2}. From our previous results,[5] we can therefore conclude that our phenomenological model is a good approximation for large r.

This conclusion agrees with intuition. Since the model was motivated by the desire to incorporate both quantum defects and the Pauli principle via supersymmetry, it is natural to suppose that the domain of validity is large distances. At small distances, however, one might expect a breakdown of the agreement with experimental observations.

In this paper we present an exploration of the small-distance behavior of the model. Our aim is to characterize the meaning of "small" and "large" distances and thereby to determine the domain of validity of the phenomenological model. We do so by studying fine-structure predictions. These are relevant to the short-distance behavior because the contribution from a Coulomb potential to the spin-orbit interaction Hamiltonian varies as r^{-3}. In fact, the model also provides contributions varying as r^{-4}, as will be seen.

We emphasize that in this paper we are exploring the small-distance properties of the phenomenological wave functions. Although we are *not* striving to better existing detailed many-body calculations, we find there is physical insight to be gained from our model.

In Sec. II, the phenomenological model is summarized and the physical content of its small-distance behavior is discussed. Section III contains the analysis of the fine structure predicted by the model. A comparison with experimental values of the doublet splittings for some alkali-metal atoms and alkali-metal-like ions is given in Sec. IV. Section V concludes. The Appendix provides an analysis of the effective charge density of the model.

II. QUANTUM-DEFECT POTENTIAL

The exactly solvable effective radial equation proposed in Ref. 5 is

$$\left[-\frac{d^2}{dy^2}-\frac{1}{y}+\frac{l^*(l^*+1)}{y^2}+\frac{1}{4n^{*2}}\right]\chi_{n^*l^*}(y)=0 . \tag{2.1}$$

Here, we are using the variable $y=\beta r$, rather than the

standard variables y/n or $y/2n$. The quantity $\beta=2\mu Z_a e^2/\hbar^2$ represents *two* inverse Bohr radii when the net charge Z_a of the atomic core is 1. Also,

$$l^*=l-\delta(l)+I(l)\ , \tag{2.2}$$

where $\delta(l)$ is the exact quantum defect and $I(l)$ is a phenomenological non-negative integer. The generalized radial wave functions $R_{n^*l^*}=\chi_{n^*l^*}/r$ have the analytical form[5]

$$R_{n^*l^*}(y)=\frac{1}{n^{*2}}\left[\frac{\beta^3\Gamma(n^*-l^*)}{2\Gamma(n^*+l^*+1)}\right]^{1/2}\left[\frac{y}{n^*}\right]^{l^*} \times e^{-y/2n^*}L_{n^*-l^*-1}^{(2l^*+1)}(y/n^*)\ , \tag{2.3}$$

where the associated Laguerre polynomials $L_{n^*-l^*-1}^{(2l^*+1)}(y/n^*)$ are defined by

$$L_n^{(\alpha)}(x)=\sum_{p=0}^{n}\frac{(-x)^p}{p!}\frac{\Gamma(n+\alpha+1)}{\Gamma(p+\alpha+1)\Gamma(n-p+1)}\ . \tag{2.4}$$

The eigenfunctions (2.3) obey the orthonormality condition

$$\int_0^\infty dr\, r^2 R_{n^*l^*}R_{n^{*\prime}l^*}=\delta_{n^*n^{*\prime}}\ . \tag{2.5}$$

For $\delta(l)=I(l)=0$, Eq. (2.1) reduces to the standard hydrogen-atom radial equation and the generalized radial wave functions reduce to the standard hydrogenic ones.

Excluding the angular-momentum barrier $l(l+1)/y^2$ and a constant, the effective potential energy $V(r)$ of this model has the form

$$V(r)=-\frac{Z_a e^2}{r}+\frac{fZ_a e^2}{r^2}\ , \tag{2.6}$$

where

$$f=\frac{1}{\beta}[l^*(l^*+1)-l(l+1)]\ . \tag{2.7}$$

Note that f may be positive, negative, or zero depending on the magnitudes of $\delta(l)$ and $I(l)$. The first term in Eq. (2.6) is the usual Coulomb interaction, while the second represents the phenomenological modifications ensuring that the eigenvalues form the Rydberg series.

The quantity of interest is the fine structure. For a single-particle system, this is determined once the external electromagnetic four-vector potential is known. We therefore desire a four-vector potential A^μ from which the effective potential of Eq. (2.6) might be derived. Physically, A^μ represents the field of the core electrons and the nucleus as taken into account by the phenomenological model.

We take A^μ to be time independent. This physical assumption treats the effective field generated by the nucleus and the core electrons in a time-averaged way. It is motivated in part by the time independence of the fine structure. Noting that the effective potential energy $V(r)$ depends only on the radial coordinate r, it then follows that A^μ is determined up to a physically irrelevant gauge transformation as[7]

$$A^\mu(r)=(\phi(r),\ \mathbf{A}(r))=((-1/e)V(r),\ \mathbf{0})\ , \tag{2.8}$$

where by definition we take $e>0$. The effective field is thus purely electrostatic.

The small-distance properties of the phenomenological model could be studied in part directly from this four-potential, by determining the charge distribution to which it corresponds. See the Appendix for details. Our primary interest, however, is in the fine-structure predictions of our model. These are explored in Sec. III.

III. FINE STRUCTURE

If a particle of charge $-e$ moves in an effective central electrostatic potential $\phi(r)$, then standard relativistic Schrödinger theory yields[8,9] a perturbing spin-orbit interaction

$$H=\frac{-e\hbar^2}{2\mu^2c^2}\frac{1}{r}\frac{d\phi}{dr}\mathbf{L}\cdot\mathbf{S}\ . \tag{3.1}$$

As the phenomenological model of Ref. 5 is effectively a one-particle system, the standard spin-orbit formalism yields the fine-structure splittings. The effective potential $V(r)$ of Eq. (2.6) gives the following fine-structure Hamiltonian:

$$H=2\mu_B^2 Z_a\left[\frac{1}{r^3}-\frac{2f}{r^4}\right]\mathbf{L}\cdot\mathbf{S}\ , \tag{3.2}$$

where $\mu_B^2=e\hbar/2\mu c$ is the Bohr magneton.

The first term in this expression generates the usual Coulomb fine structure, proportional to r^{-3}. However, there is also a term proportional to r^{-4}. This radial dependence is normally associated with corrections due to core dipole polarization.[10] Contributions from this term tend to zero for large values of l because both δ and I tend to zero in that limit. This result is also in agreement with core-polarization calculations.[11] Furthermore, since the usual effects of core polarizability are automatically taken into account in n^*, the extra term in the potential may be viewed as an effective correction for low-lying states that compensates for the use of exact quantum-defect theory in the phenomenological model. It is intriguing to find such a term naturally present.

The first-order energy shift is the expectation of the perturbing Hamiltonian. The angular expectation $\xi(j,l,s)$ is determined[8,9] by the properties of the spherical harmonics:

$$\xi(j,l,s):=\langle jmls\mid\mathbf{L}\cdot\mathbf{S}\mid jmls\rangle =\tfrac{1}{2}[j(j+1)-l(l+1)-s(s+1)]\ . \tag{3.3}$$

As usual, this means that all levels except the ^2S ones are split into doublets.

Determination of the radial expectation $\zeta(n,l)$ is more involved. Let us first recall the situation according to standard lore. Typically, the effective central potential and the radial functions are not explicitly known. For this case, Landé gave[12] a semiempirical formula for the radial expectation

$$\zeta(n,l) := \langle nl \mid Z_a r^{-3} \mid nl \rangle = \frac{\beta^3}{8} \frac{Z_a^2 Z_i^2}{n^{*3}[l(l+\frac{1}{2})(l+1)]} . \quad (3.4)$$

Here, Z_a is the net charge of the nucleus and the electron core, and Z_i is an effective inner charge usually treated as a parameter. This formula may be derived from simple assumptions about the screening properties of the core.[13] It reduces to the correct answer for a purely Coulomb central potential with a nuclear charge Z when Z_a and Z_i are replaced by Z and n^* is replaced by n. Combined with Eq. (3.3), the formula correctly gives the basic regularities of the alkali-atom spectra. In particular, the Landé formula yields a doublet splitting ΔE_L given by

$$\Delta E_L = \frac{Z_i^2 Z_a^2}{n^{*3} l(l+1)} \alpha^2 I_\infty , \quad (3.5)$$

where $I_\infty = \mu e^4/2\hbar^2$ is the ionization potential of hydrogen and $\alpha = e^2/\hbar c$ is the fine-structure constant.

In our case, both the effective central potential and the radial eigenfunctions are explicitly provided. It is therefore possible to evaluate analytically the first-order energy shift, using Eq. (3.2). Defining

$$\zeta^*(n^*,l^*) = 2\mu_B^2 Z_a \left\langle n^* l^* \left| \left[\frac{1}{r^3} - \frac{2f}{r^4} \right] \right| n^* l^* \right\rangle , \quad (3.6)$$

the model gives first-order energy-level corrections

$$\delta E(n^*,l^*) = \xi(j,l,s)\zeta^*(n^*,l^*) . \quad (3.7)$$

The doublet splitting ΔE in this case is therefore

$$\Delta E = \Delta E_3 + \Delta E_4 , \quad (3.8)$$

where

$$\Delta E_3 = 8(l+\tfrac{1}{2})\langle n^* l^* \mid y^{-3} \mid n^* l^* \rangle Z_a^4 \alpha^2 I_\infty ,$$
$$\Delta E_4 = -16\beta f (l+\tfrac{1}{2})\langle n^* l^* \mid y^{-4} \mid n^* l^* \rangle Z_a^4 \alpha^2 I_\infty . \quad (3.9)$$

The general matrix element for y^d with arbitrary d was explicitly evaluated in terms of Γ functions in Ref. 5, Eq. (11). For $l_i^* = l_f^* = l^*$, and $n_i^* = n_f^* = n^*$, this result determines all needed expectation values. Alternatively, the expectation of y^d can be found by direct computation. Thus, from Eq. (2.3) and changing variables to $x = y/n^*$, we find

$$X := \langle n^* l^* \mid y^d \mid n^* l^* \rangle = \tfrac{1}{2} n^{*(d-1)} \frac{\Gamma(n^*-l^*)}{\Gamma(n^*+l^*+1)} \times \int_0^\infty dx\, x^{2l^*+2+d} e^{-x} [L_{n^*-l^*-1}^{2l^*+1}(x)]^2 . \quad (3.10)$$

The integral in this equation is of a type that has been evaluated in Ref. 14, Eq. (2.13). After minor rearrangement, this gives

$$X = \tfrac{1}{2} n^{*(d-1)} \sum_{k=0}^{n^*-l^*-1} (-1)^k \frac{\Gamma(n^*-l^*-2-d-k)\Gamma(2l^*+3+d+k)}{\Gamma(n^*-l^*-k)\Gamma(2l^*+2+k)\Gamma(k+1)\Gamma(-1-d-k)} . \quad (3.11)$$

Note that the integral is well defined only for $(2l^*+3+d) > 0$. Given $\delta(l)$, this constraint can exclude certain values of I.

In particular, the result (3.11) yields an explicit closed formula for the expectation value of y^{-3}. We find

$$\langle n^* l^* \mid y^{-3} \mid n^* l^* \rangle = \frac{1}{8n^{*3}[l^*(l^*+\frac{1}{2})(l^*+1)]} . \quad (3.12)$$

Using this result, the doublet splitting contribution ΔE_3 of Eq. (3.9) is found to be

$$\Delta E_3 = \frac{(l+\frac{1}{2})}{n^{*3} l^*(l^*+\frac{1}{2})(l^*+1)} Z_a^4 \alpha^2 I_\infty . \quad (3.13)$$

This is just the expression ΔE_L of Eq. (3.5) with an effective inner charge Z_i^* given explicitly by

$$Z_i^* = \left[\frac{l(l+\frac{1}{2})(l+1)}{l^*(l^*+\frac{1}{2})(l^*+1)} \right]^{1/2} Z_a . \quad (3.14)$$

We see that our phenomenological model naturally incorporates the Landé formula. The replacement of l in Eq. (3.4) by l^* in Eq. (3.12) is absorbed in the definition of the effective inner charge Z_i^*. The important feature is the n^{*3} dependence, which is present in both equations. This unexpected result further confirms the validity of the model.

IV. COMPARISON WITH EXPERIMENT

To investigate the short-distance validity of the model, the formulas presented in Sec. III can be used to determine fine-structure splittings for the alkali-metal atoms lithium and sodium and for the alkali-metal-like singly ionized beryllium and magnesium ions. These results can be compared to experimentally determined values where available.[15] For the most part, these include the low-lying p and d levels. Hydrogen and singly ionized helium are not considered, because for these systems the model reduces to the standard case.

Table I shows the values of the quantum defect $\delta(l)$ (Ref. 2) and the phenomenological integer $I(l)$ used for various values of l. The predicted effective charge Z_i^* given by Eq. (3.14) is also shown, as is the value of $2\beta f$.

Note that the values of the integer $I(l)$ taken are forced upon us by the conditions for existence of the integral (3.10) and of the associated Laguerre polynomials of Eq. (2.3).[5] These values are precisely the ones neces-

TABLE I. For different values of the quantum number l, we list the values of the parameters δ, I, Z_i^*, and $2\beta f$ that were used in calculating ΔE_3 and ΔE for the states listed in Tables II–V.

l	Parameter	Li	Be II	Na	Mg II
1	δ	0.05	0.051	0.859	0.702
	I	0	0	1	1
	Z_i^*	1.057	2.116	0.865	1.496
	$2\beta f$	−0.295	−0.301	+0.886	+1.966
2	δ	0	0.003	0.01	0.047
	I	0	0	0	0
	Z_i^*	1	2.004	1.006	2.060
	$2\beta f$	0	−0.030	−0.100	−0.466
3	δ		0.001		
	I		0		
	Z_i^*		2		
	$2\beta f$		−0.014		

sary in the supersymmetric picture.[5]

Note also that the quantity $2\beta f$ is negative for most cases with nonzero quantum defect. From Eq. (A1) of the Appendix, it follows that the phenomenological potential in these cases describes a charge distribution that is a reasonable approximation to the physical situation: there is a positive charge at the origin and a negative charge distribution over all space. In contrast, for the supersymmetric cases of the p levels of Na and Mg II, there is a positive distribution over all space. As has been shown elsewhere,[3–5] the resulting large-distance behavior is just what is needed to incorporate the quantum defects and the Pauli principle. However, on physical grounds it would be surprising if the small-distance behavior as exhibited by the fine-structure splittings for these cases were also in agreement with experiment.

First, consider the case of lithium. Table II shows the values of $(Z_a/Z_i)^2\Delta E_L$, ΔE_3, and ΔE, as calculated from Eqs. (3.5), (3.8), and (3.9), and the experimental values ΔE_{expt} taken from Ref. 15. The model shows good agreement with experiment. In detail, the values of ΔE_3 seem to be in best agreement; the contribution of ΔE_4 is of the wrong sign for the p levels and is zero for the d levels. This means that the Landé formula with $Z_i = Z_a$ may be expected to give better agreement. For certain values, the experimental results are not available in Ref. 15. Given the agreement of the known levels, the theoretical values shown may be viewed as predictions to be tested by future experiment.

Next, consider the lithium-like ion Be II. Table III shows the same information for this case. The agreement here is again good, with the exception of the inverted $4p$ levels. Again, in this case the contribution from ΔE_4 is of the wrong sign. Note that the splitting predictions become more precise as the value of n increases, i.e., as the valence electron spends less time near the origin. This is in agreement with the notion that the phenomenological wave functions provide a good picture away from the origin.

The results for sodium are provided in Table IV. For

TABLE II. Theoretical and experimental values of the fine-structure splittings for lithium. The units are inverse centimeters. Values of $(Z_a/Z_i)^2\Delta E_L$, ΔE_3, and ΔE are derived from Eqs. (3.5), (3.8), and (3.9). Values of ΔE_{expt} are taken from Ref. 15.

Li orbital	$(Z_a/Z_i)^2\Delta E_L$	ΔE_3	ΔE	ΔE_{expt}
$2p$	0.394	0.440	0.514	0.336
$3d$	0.036	0.036	0.036	0.04
$4d$	0.015	0.015	0.015	0.02
$5d$	0.0078	0.0078	0.0078	0.01
$6d$	0.0045	0.0045	0.0045	
$7d$	0.0028	0.0028	0.0028	
$8d$	0.0019	0.0019	0.0019	

TABLE III. Theoretical and experimental values of the fine-structure splittings for singly ionized beryllium. The units are inverse centimeters. Values of $(Z_a/Z_i)^2\Delta E_L$, ΔE_3, and ΔE are derived from Eqs. (3.5), (3.8), and (3.9). Values of ΔE_{expt} are taken from Ref. 15.

Be II orbital	$(Z_a/Z_i)^2\Delta E_L$	ΔE_3	ΔE	ΔE_{expt}
$2p$	6.31	7.06	8.29	6.58
$3p$	1.82	2.04	2.43	1.92
$4p$	0.76	0.85	1.01	−0.22
$5p$	0.39	0.43	0.52	0.44
$3d$	0.58	0.58	0.58	0.55
$4d$	0.24	0.24	0.25	0.24
$5d$	0.12	0.13	0.13	0.12
$6d$	0.072	0.072	0.073	
$7d$	0.046	0.046	0.046	
$8d$	0.030	0.031	0.031	
$4f$	0.12	0.12	0.12	0.12
$5f$	0.062	0.062	0.063	0.06
$6f$	0.036	0.036	0.036	
$7f$	0.023	0.023	0.023	
$8f$	0.015	0.015	0.015	

TABLE IV. Theoretical and experimental values of the fine-structure splittings for sodium. The units are inverse centimeters. Values of $(Z_a/Z_i)^2\Delta E_L$, ΔE_3, and ΔE are derived from Eqs. (3.5), (3.8), and (3.9). Values of ΔE_{expt} are taken from Ref. 15.

Na orbital	$(Z_a/Z_i)^2\Delta E_L$	ΔE_3	ΔE	ΔE_{expt}
3*p*	0.296	0.226	0.151	17.196
4*p*	0.090	0.071	0.045	5.63
5*p*	0.041	0.031	0.019	2.52
6*p*	0.022	0.016	0.010	1.25
7*p*	0.013	0.0094	0.0058	0.74
8*p*	0.0080	0.0060	0.0037	0.47
9*p*	0.0054	0.0041	0.0025	0.47
3*d*	0.036	0.037	0.037	−0.049
4*d*	0.015	0.016	0.016	−0.035
5*d*	0.0078	0.0079	0.0080	−0.024
6*d*	0.0045	0.0046	0.0047	−0.023

the *np* levels, the predicted splittings are too small by about two orders of magnitude. It is interesting to note that this is the case for the Landé formula also. This is normally explained as being due to core penetration by the valence electron and is corrected by the phenomenological effective inner charge Z_i. The *nd* levels are experimentally found to be inverted, which is unexplained by either the Landé formula or the model. Note again that the model contribution from ΔE_4 is of the wrong sign and magnitude. As anticipated above, the unphysical nature of the charge distribution in this case leads to poor predictions. This is what we are looking for: evidence of a breakdown of the phenomenological model.

A similar situation holds for the sodium-like ion Mg II. See Table V. The *np* splittings are too small by about two orders of magnitude, as is the Landé splitting in the absence of the effective inner charge Z_i. Once again, this is the situation where the model yields an unphysical charge distribution near the origin and so poor results are to be expected. Just as for sodium, the *nd* splittings are inverted.

TABLE V. Theoretical and experimental values of the fine-structure splittings for singly ionized magnesium. The units are inverse centimeters. Values of $(Z_a/Z_i)^2\Delta E_L$, ΔE_3, and ΔE are derived from Eqs. (3.5), (3.8), and (3.9). Values of ΔE_{expt} are taken from Ref. 15.

Mg II orbital	$(Z_a/Z_i)^2\Delta E_L$	ΔE_3	ΔE	ΔE_{expt}
3*p*	3.85	2.15	1.00	91.57
4*p*	1.30	0.73	0.29	30.52
5*p*	0.58	0.33	0.12	13.80
6*p*	0.31	0.18	0.064	7.38
7*p*	0.19	0.068	0.037	4.41
8*p*	0.12	0.067	0.024	2.84
9*p*	0.082	0.046	0.016	1.93
3*d*	0.60	0.64	0.68	−0.87
4*d*	0.25	0.27	0.28	−0.52
5*d*	0.13	0.14	0.14	+0.30
6*d*	0.074	0.078	0.084	−0.16
7*d*	0.046	0.049	0.052	−0.10
8*d*	0.031	0.033	0.035	−0.06

V. CONCLUSION

In this paper, we have investigated the short-distance behavior of a supersymmetry-inspired phenomenological model in an effort to characterize its domain of validity. We have done so by examining the fine-structure splittings given by the model. These are relevant to the short-distance behavior because they vary as r^{-3} and r^{-4} in the model.

The phenomenological potential is found to incorporate the n^* dependence of the Landé formula. Furthermore, for finite results the model requires supersymmetric values of the phenomenological integer $I(l)$.

The numerical agreement with experimental values of the splittings is good for the light alkali-like atoms lithium and singly ionized beryllium. In contrast, the numerical agreement fails for the heavier alkali-like atoms sodium and singly ionized magnesium. Thus, we have successfully identified the domain of validity of our phenomenological model.

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APPENDIX: EFFECTIVE CHARGE DENSITY

The effective charge density $\rho(\mathbf{r})$ associated with the effective potential energy $V(r)=-\phi(r)/e$ of Eq. (2.6) is

$$4\pi\rho(\mathbf{r})=-\nabla^2\phi(r)$$

$$=4\pi Z_a e\delta^3(\mathbf{r})-8\pi Z_a ef\frac{\delta^3(\mathbf{r})}{r}+\frac{2Z_a ef}{r^4}\ . \qquad \text{(A1)}$$

The integral over all space of this density gives a total charge of +1, as it should.

The first term of this charge distribution represents a unit positive point charge at the origin. The effects of the contributions of the two other terms are determined by the sign of f. When f is negative, the expression (A1) may be viewed as a reasonable approximation to the physical distribution in that there is a positive charge at the origin and a negative charge density over all space.

However, when f is positive, the last term of Eq. (A1) represents a positive charge density over all space. In

particular, this situation can occur for nonzero values of the phenomenological integer I. Recall that our effective radial equation was motivated by the large-distance behavior of the valence electron and by the incorporation via supersymmetry of the Pauli exclusion principle. The nuclear charges and the electron-core charges are thereby treated in an approximation for which there is no reason, *a priori*, to expect a physical charge density. It is the limitations of this approximation that are probed in the present paper.

We remark that, for the case of negative f, the above analysis suggests a simple modification of the potential that leaves unchanged the desirable large-distance properties but that has an even more physical interpretation near the origin. First, note that in terms of an ϵ ball about the origin the charge distribution $\rho(\mathbf{y})$ of Eq. (A1) can be viewed as the limit as $\epsilon\to 0$ of the distribution $\rho(\mathbf{y},\epsilon)$ given by

$$4\pi\rho(\mathbf{y},\epsilon)=\begin{cases}4\pi Z_a e\left[1-\dfrac{2f}{\epsilon}\right]\delta^3(\mathbf{y}), & y=0\\ 0, & 0<y<\epsilon\\ \dfrac{2Z_a e f}{y^4}, & \epsilon<y\ .\end{cases} \tag{A2}$$

Next, note that this new distribution can be perturbed to another, $\tilde{\rho}(\mathbf{y},\epsilon)$, that represents Z nuclear charges at the origin while maintaining the successful large-distance behavior of the charge distribution. Near the origin, the perturbed distribution must then be given by some function constrained by the requirement that the total charge of the system is finite and equal to Z_a. For simplicity, we choose this function as a constant. This completely specifies the charge distribution.

Explicitly, the charge density $\tilde{\rho}(\mathbf{y},\epsilon)$ is now given by

$$4\pi\tilde{\rho}(\mathbf{y},\epsilon)=\begin{cases}4\pi Z Z_a e\left[1-\dfrac{2f}{\epsilon}\right]\delta^3(\mathbf{y}), & y=0\\ -\left[\dfrac{3}{4}\right]^4\dfrac{(Z-1)Z_a e}{\epsilon^3}, & 0<y<\frac{4}{3}\epsilon\\ \dfrac{-(Z-1)Z_a e\epsilon}{y^4}, & \frac{4}{3}\epsilon<y\ ,\end{cases} \tag{A3}$$

where

$$2Z_a f=(Z-Z_a)\epsilon\ . \tag{A4}$$

This new distribution yields a potential that is a perturbation on the phenomenological potential (2.6). Since the large-distance behavior is unchanged, the successful predictions for the transition probabilities given in Ref. 5 remain unaffected for small enough ϵ. However, the short-range behavior and hence quantities such as the fine structure will typically be modified.

This perturbation potential could be used for a phenomenological approach to the fine-structure splittings. Then, ϵ becomes a free parameter playing a role analogous to that of Z_i for the Landé formula. Unlike Z_i, however, it has a direct physical meaning as the effective core radius. This radius could be estimated by comparison of numerical predictions of the model with experimental data.

Note that the perturbation has the desired physical interpretation for negative f only. Also, for positive f the prescription provided does *not* uniquely establish the charge distribution.

Since our goal here is not a new phenomenological description of the fine-structure splittings in terms of model charge distributions but rather an investigation of the range of validity of our established model, we do not pursue this idea in the present work.

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