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PAPER

Multiscale quantum-defect theory and its application to atomic spectrum

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Abstract

We present a multiscale quantum-defect theory based on the first analytic solution for a two-scale long range potential consisting of a Coulomb potential and a polarization potential. In its application to atomic structure, the theory extends the systematic understanding of atomic Rydberg states, as afforded by the standard single-scale quantum-defect theory, to a much greater range of energies to include the first few excited states and even the ground state. Such a level of understanding has important implications not only on atomic structure, but also on the electronic structure of molecules and on atomic and molecular interactions and reactions. We demonstrate the theory by showing that it provides an analytic description of the energy variations of the standard Coulomb quantum defects for alkali-metal atoms.

1. Introduction

The Rydberg–Ritz formula [1, 2] for atomic spectra

$$(E_{nlj} - E_{\text{ion}})/R_M = -\frac{1}{(n - \mu_{lj}^{\text{Coul}})^2},$$

(1)

was one of the very first universal properties uncovered for quantum systems, and played an important role in the very establishment of the quantum theory. Here E_{ion} represents the ionization energy, $R_M = R_\infty/(1 + m_e/M)$ is the reduced mass Rydberg constant (with M (m_e) being the ion (electron) mass and R_∞ being the Rydberg constant), n is the principle quantum number, l and j are the orbital and total angular momenta of the electron, respectively. The formula asserts that despite considerable differences in atomic spectra, the Rydberg series for different atoms differ from each other only in a Coulomb quantum defect μ_{lj}^{Coul} which encapsulates all complexities of short-range interactions. This universality, which originates from the fact that a sufficiently highly excited electron sees mostly the Coulomb potential, stimulated the development of the quantum-defect theory (QDT) and multichannel QDT [3–6]. They have long become the standard for understanding atomic and molecular spectra and electron-ion interactions [3–7].

The universality as represented by the Rydberg–Ritz formula with a constant μ_{lj}^{Coul} is however strictly applicable only to sufficiently highly excited Rydberg states. This is reflected, especially for atoms with highly polarizable cores, by a significant n dependence of μ_{lj}^{Coul} for lower lying states (see, e.g., [8–11]). Does there exist a more general universality that applies also to the first few excited states or even the ground state, which are often of more practical and experimental interest? The answer to this question has implications far beyond atomic structure. Not only will it determine the degree to which other single-atom properties, such as oscillator

strengths, ionization cross sections, static and dynamic polarizabilities (see, e.g., [12]), follow universal behaviors outside of the Rydberg regime. It will also determine the degree to which important atomic interaction parameters, such as the C_6 van der Waals coefficients (see, e.g., [13]), follow universal behaviors for different atoms and different electronic states. Even further, it will determine the relations among different electronic states of a molecule and the relations among electronic states of different molecules. The prospect for such systematic understanding of an entire manifold of molecular electronic states can be crucial for understanding atomic and molecular interactions and reactions, especially in excited electronic states where many of them participate simultaneously.

This work establishes a broader universality in atomic structure as the first application of an analytic *two-scale* QDT. The theory is based on our analytic solution for the 'Coulomb+polarization' potential of the form $-C_1/r - C_4/r^4$. It is, to the best of our knowledge, the first analytic solution of the Schrödinger equation for a two-scale central potential, for which no analytic solution is previously known or expected. Our solution represents a new class of special functions and has potential for generalization to other multiscale potentials. In applying the two-scale QDT to atomic structure, we show that the theory introduces a 'new' quantum defect that has much weaker energy dependence than the traditional Coulomb quantum defects μ^{Coul} that goes into the Rydberg–Ritz formula, and the theory provides an analytic description of the n dependence of μ^{Coul} for Rb and Cs atoms, down to their ground states. The results establishes, in an analytic framework, a broader universality in atomic structure and spectra. Physically, it means that the statement that a Rydberg electron sees mostly the Coulomb potential can be replaced by a more general statement that an excited or an outer electron sees mostly a Coulomb potential plus a polarization potential, to a remarkable accuracy.

We note that the importance of polarization in atomic structure is well known, as reflected both in perturbation calculations for alkali metals [14, 15], and in model potentials chosen, e.g., both for 'one-electron' alkali atoms [16, 17] and for 'two-electron' alkaline Earth atoms [5, 18]. The underlying universality was however difficult to identify, define, or describe, since a perturbative treatment is only applicable to high angular momentum states, and the effect of core polarization is difficult to distinguish from other short-range effects in a numerical calculation.

2. Two-scale QDT

Our two-scale QDT for 'Coulomb+polarization' potential is built upon the analytic solution of the radial Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{C_1}{r} - \frac{C_4}{r^4} - \epsilon \right] v_{\epsilon l}(r) = 0, \tag{2}$$

where μ is the reduced mass, $C_1 > 0$ and $C_4 > 0$ measure the strengths of the Coulomb and the polarization potentials, respectively. The equation has two characteristic length scales $\beta_n := (2\mu C_n/\hbar^2)^{1/(n-2)}$ ($n = 1, 4$), corresponding to each one of the potential terms of the form of $-C_n/r^n$ ($n = 1, 4$). Each length scale β_n has a corresponding energy scale of $s_E^{(n)} = (\hbar^2/2\mu)(1/\beta_n)^2$. Scaling the radius r by β_1, and the energy ϵ by its corresponding $s_E^{(1)}$, the scaled Schrödinger equation takes the form of

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r_s^2} - \frac{l(l+1)}{r_s^2} + \frac{1}{r_s} + (\beta_4/\beta_1)^2 \frac{1}{r_s^4} + \epsilon_s \right] v_{\epsilon_s l}(r_s) = 0, \tag{3}$$

where $r_s := r/\beta_1$ and $\epsilon_s := \epsilon/s_E^{(1)}$, with the ratio of length scales β_4/β_1 serving as a measure of the relative strength of the Coulomb and the polarization potentials.

Through generalizations of techniques that have led to other single-scale QDT solutions for $1/r^6$ [19], $1/r^3$ [20], and $1/r^4$ [21–25] potentials, we have solved equation (3) analytically to obtain its QDT base pair of solutions and the corresponding QDT functions. The base pair f^c and g^c [26] are defined with energy and partial wave independent [27] asymptotic behaviors around the origin (specifically $r_s \ll \beta_4/\beta_1$),

$$f_{\epsilon_s l}^c(r_s) \sim r_s \sqrt{\frac{2}{\pi(\beta_4/\beta_1)}} \cos[(\beta_4/\beta_1)/r_s - \pi/4], \tag{4}$$

$$g_{\epsilon_s l}^c(r_s) \sim -r_s \sqrt{\frac{2}{\pi(\beta_4/\beta_1)}} \sin[(\beta_4/\beta_1)/r_s - \pi/4], \tag{5}$$

for all energies ϵ_s. They are normalized such that their Wronskian $W(f^c, g^c) := f^c(\mathrm{d}g^c/\mathrm{d}r_s) - (\mathrm{d}f^c/\mathrm{d}r_s)g^c = 2/\pi$. For $\epsilon_s < 0$, the QDT base pair has asymptotic behavior at large r_s given by

$$f_{\epsilon_s l}^c(r_s) \stackrel{r_s \to \infty}{\sim} \frac{1}{\sqrt{\pi\kappa_s}}[W_{f+}^c(2\kappa_s r_s)^{1/(2\kappa_s)}e^{-\kappa_s r_s} + W_{f-}^c(2\kappa_s r_s)^{-1/(2\kappa_s)}e^{+\kappa_s r_s}], \tag{6}$$

$$g_{\epsilon_s l}^c(r_s) \overset{r_s \to \infty}{\sim} \frac{1}{\sqrt{\pi \kappa_s}} [W_{g+}^c (2\kappa_s r_s)^{1/(2\kappa_s)} e^{-\kappa_s r_s} + W_{g-}^c (2\kappa_s r_s)^{-1/(2\kappa_s)} e^{+\kappa_s r_s}], \tag{7}$$

where $\kappa_s = (-\epsilon_s)^{1/2}$. It gives a 2×2 W^c matrix with elements W_{xy}^c describing the evolution of a wave function through the $-C_1/r - C_4/r^4$ potential at negative energies.

In terms of the W^c elements, the bound spectra for any potential $V(r)$ that behaves asymptotically as $-C_1/r - C_4/r^4$ can be formulated [26] as the solutions of

$$\chi_l^c(\epsilon_s, \beta_4/\beta_1) = K^c(\epsilon, l, j). \tag{8}$$

Here $\chi_l^c = W_{f-}^c/W_{g-}^c$ is a universal function of the scaled energy ϵ_s and the ratio of length scales β_4/β_1. The K^c is a short-range K matrix defined by matching the short-range wave function, $u_{\epsilon l j}(r)$ for potential $V(r)$, to a linear combination of the QDT base pair [26, 27]

$$u_{\epsilon l j}(r) = A_{\epsilon l j}[f_{\epsilon_s l}^c(r_s) - K^c(\epsilon, l, j)g_{\epsilon_s l}^c(r_s)], \tag{9}$$

at any radius where $V(r)$ has become well represented by $-C_1/r - C_4/r^4$. Compared to single-scale QDT formulations [26], the formula for bound spectra in the two-scale formulation, equation (8), is structurally the same except that the two-scale χ_l^c depends parametrically on β_4/β_1, and the two-scale K^c is defined in reference to $-C_1/r - C_4/r^4$, instead of $-C_1/r$ solutions.

From our analytic solutions, we obtain

$$\chi_l^c = \frac{\tan\theta_l^- + \tan(\pi\nu/2)(1 + \widetilde{M_l})/(1 - \widetilde{M_l})}{1 - \tan\theta_l^- \tan(\pi\nu/2)(1 + \widetilde{M_l})/(1 - \widetilde{M_l})}. \tag{10}$$

Here ν is the characteristic exponent for the $-1/r_s - (\beta_4/\beta_1)^2/r_s^4$ potential, given in the appendix. It is a function of the scaled energy ϵ_s and depends parametrically on β_4/β_1, as are the $\tan\theta_l^-$ and $\widetilde{M_l}$ functions in equation (10). The function $\tan\theta_l^-$ is given by $\tan\theta_l^- = Y_l^-/X_l^-$, with $X_l^- = \sum_{j=-\infty}^{\infty}(-1)^j b_{2j}^-$, and $Y_l^- = \sum_{j=-\infty}^{\infty}(-1)^j b_{2j+1}^-$. Here b_m^-s are the coefficients of the generalized Neumann expansion [19, 28] of a wave function. They are given by $b_0^- = 1$, and

$$b_m^- = \Delta^m \frac{\Gamma(\nu)\Gamma(\nu + \nu_0 + 1)\Gamma(\nu - \nu_0 + 1)}{\Gamma(\nu - w^-)} \times \frac{\Gamma(\nu + m - w^-)}{\Gamma(\nu + m)\Gamma(\nu + \nu_0 + m + 1)\Gamma(\nu - \nu_0 + m + 1)} c_m(\nu), \tag{11}$$

$$b_{-m}^- = (-1)^m \Delta^m \frac{\Gamma(\nu + 1 + w^-)}{\Gamma(\nu + 1)\Gamma(\nu + \nu_0)\Gamma(\nu - \nu_0)} \times \frac{\Gamma(\nu - m + 1)\Gamma(\nu + \nu_0 - m)\Gamma(\nu - \nu_0 - m)}{\Gamma(\nu + 1 + w^- - m)} c_m(-\nu), \tag{12}$$

in which $\Gamma(x)$ represents the gamma function, m is a positive integer, $\nu_0 := l + 1/2$, $\Delta := (\beta_4/\beta_1)\sqrt{-\epsilon_s}$, $w^- := -1/2 + 1/(2\sqrt{-\epsilon_s})$, and $c_m(\nu) := \prod_{j=0}^{m-1} Q(\nu + j)$ with $Q(\nu)$ given by a continued fraction

$$Q(\nu) = \frac{1}{1 - \left(\frac{\beta_4}{\beta_1}\right)^2 \frac{(\nu + 3/2)^2 \epsilon_s + 1/4}{(\nu + 1)[(\nu + 1)^2 - \nu_0^2](\nu + 2)[(\nu + 2)^2 - \nu_0^2]} Q(\nu + 1)}. \tag{13}$$

The $\widetilde{M_l}$ function in equation (10) is given by $\widetilde{M_l} := [\Gamma(\nu - w^-)/\Gamma(-\nu - w^-)]M_l$, where

$$M_l := [(\beta_4/\beta_1)^2|\epsilon_s|]^\nu \frac{\Gamma(1 - \nu)\Gamma(1 - \nu + \nu_0)\Gamma(1 - \nu - \nu_0)}{\Gamma(1 + \nu)\Gamma(1 + \nu + \nu_0)\Gamma(1 + \nu - \nu_0)} \left(\frac{C_l(-\nu)}{C_l(+\nu)}\right), \tag{14}$$

in which $C_l(\nu) := \prod_{j=0}^{\infty} Q(\nu + j)$.

3. Application to bound spectra of Cs and Rb

Equation (8) gives the two-scale QDT spectrum as the cross points between a universal function $\chi_l^c(\epsilon_s, \beta_4/\beta_1)$ and a short-range $K^c(\epsilon, l, j)$ function. It can also be formulated in a μ^c representation [25], as $\chi_l^\mu(\epsilon_s, \beta_4/\beta_1) = \mu^c(\epsilon, l, j)$, where $\chi_l^\mu := [\tan^{-1}(\chi_l^c) - \pi/4]/\pi$ and μ^c is the 'new' quantum defect defined by $\mu^c := [\tan^{-1}(K^c) - \pi/4]/\pi$. Both χ_l^μ and μ^c are taken to be within a range of $[0, 1)$ by taking $\tan^{-1}(x)$ to be within a range of $[\pi/4, 5\pi/4)$. In applying equation (8) to the spectra of an alkali atom, one has $C_1 = 1$ and $C_4 = \alpha_{\text{core}}/2$ in atomic units, where α_{core} is the polarizability of the core (i.e. the ionic core excluding the outer electron), and $\beta_4/\beta_1 = 2\mu^{3/2}\sqrt{\alpha_{\text{core}}}$.

The key difference between the two-scale QDT and the standard single-scale QDT [3, 5] lies in the fact that the 'new' quantum defect μ^c, being defined in reference to the $-C_1/r - C_4/r^4$ potential, is determined by the logarithmic derivative of a wave function at much shorter distances than the standard quantum defect μ_{lj}^{Coul} defined in reference to the $-C_1/r$ Coulomb potential, and has therefore much weaker energy dependence.

Figure 1. The μ^c representation of the multiscale QDT bound spectra, as the crossing points between $\chi_l^\mu(\epsilon_s, \beta_4/\beta_1)$ (the curves plotted) and μ^c (the nearly horizontal lines) as functions of energy, illustrated here for $^2S_{1/2}$ ($l = 0$) series of Cs (Black) and Rb (Blue). When the spectrum is known, the function χ_l^μ evaluated at bound state energies gives a discrete representation of the μ^c function. Here we use the experimental data for Cs [9] and Rb [11, 29] (squares) to show that μ^c, and therefore K^c, are to a very good approximation a constant, including those for the ground states (6s for Cs and 5s for Rb). The χ^μ as a function of energy is different for Cs and Rb due to their different length scale ratios β_4/β_1, which in turn is due primarily to their different core polarizabilities. α_{core} is taken here to be 15.77 a.u. [9] for Cs, and 9.076 a.u. for Rb [15].
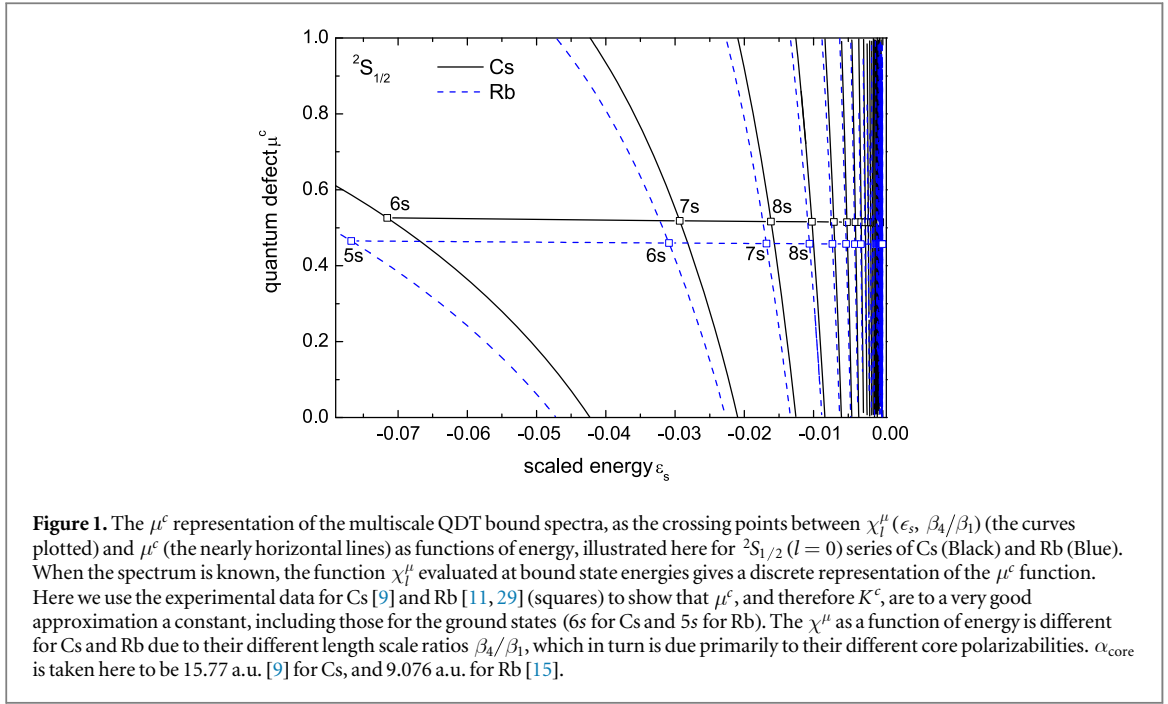
Figure 1 illustrates both the μ^c representation [25] of the two-scale QDT spectrum, and the weak energy dependence of $\mu^c(\epsilon, l, j)$, using experimental data for the $^2S_{1/2}$ series of both Cs [9] and Rb [11, 29].

From a different perspective, the two-scale QDT provides an analytic description of the energy dependence of the μ_{lj}^{Coul} in the Rydberg–Ritz formula. Specifically, equation (8) for the bound spectra can be solved, more precisely re-casted, as the solutions of

$$\epsilon_{nljs} = -\frac{1}{4[n - \mu_{lj}^{\text{Coul}}(\epsilon_{nljs})]^2}. \tag{15}$$

Here ϵ_{nljs} is a scaled bound state energy (hence the subscript s) defined by $\epsilon_{nljs} := (E_{nlj} - E_{\text{ion}})/s_E^{(1)} = (E_{nlj} - E_{\text{ion}})/4R_M$,

$$\tan(\pi\mu_{lj}^{\text{Coul}}) = -\frac{1 - t_l}{1 + t_l} \tan[\pi(\nu - 1/2)], \tag{16}$$

with

$$t_l = \left[\frac{\Gamma(1/(2\kappa_s) + \nu + 1/2)}{\Gamma(1/(2\kappa_s) - \nu + 1/2)} M_l\right] \frac{K^c \cos(\pi\nu/2 - \theta_l^-) + \sin(\pi\nu/2 - \theta_l^-)}{K^c \cos(\pi\nu/2 + \theta_l^-) - \sin(\pi\nu/2 + \theta_l^-)}. \tag{17}$$

Equation (15), which is formally equivalent to equation (1) with a different scaling, shows that the spectra for any potential that behaves asymptotically as $-C_1/r - C_4/r^4$ can be expressed as a Rydberg–Ritz formula with an energy-dependent μ_{lj}^{Coul}, consistent with the general conclusion by Hartree many years ago [2]. The energy dependence is described analytically by equation (16). It is, to the best of our knowledge, the first nonperturbative analytic description of this energy dependence.

Figure 2 compares the Coulomb quantum defects μ_{lj}^{Coul} to the two-scale QDT predictions of equation (16) with a *constant* K^c, using as examples the $^2S_{1/2}$ and $^2P_{1/2}$ series of Rb and Cs. The Rb data are taken from recent precision measurement and analysis in [8, 11, 29]. The α_{core} is taken to be 9.076 a.u. [15]. The dimensionless parameter K^c is determined to be -1.314 for the $^2S_{1/2}$ series, and -1.173 for the $^2P_{1/2}$ series, by fitting to an intermediate-n portion of the spectra. They correspond to $\mu^c = 0.4571$ for the $^2S_{1/2}$ series, and $\mu^c = 0.4747$ for the $^2P_{1/2}$ series. The Cs spectrum data are from [9], and we have taken its $\alpha_{\text{core}} = 15.77$ a.u. [9]. The parameters K^c are determined to be -0.9135 for the $^2S_{1/2}$ series, and -0.8942 for the $^2P_{1/2}$ series. They correspond to $\mu^c = 0.5144$ and $\mu^c = 0.5178$ for the $^2S_{1/2}$ and $^2P_{1/2}$ series, respectively. It is remarkable that even with such constant K^cs (or μ^cs), the two-scale QDT predicts μ_{lj}^{Coul} with an accuracy better than 0.3% for the ground states, and the energy with an accuracy better than 1.3% for the ground states, and progressively better for excited states.

We note that the atomic spectra differ from those of diatomic rovibrational spectra [27] in that the quantum defect, K^c or μ^c, does depend strongly on the partial wave l, and for heavy atoms such as Rb and Cs, also on j. The sensitive l dependence, already well known in standard QDT for μ_{lj}^{Coul}, is due to the small electron mass which
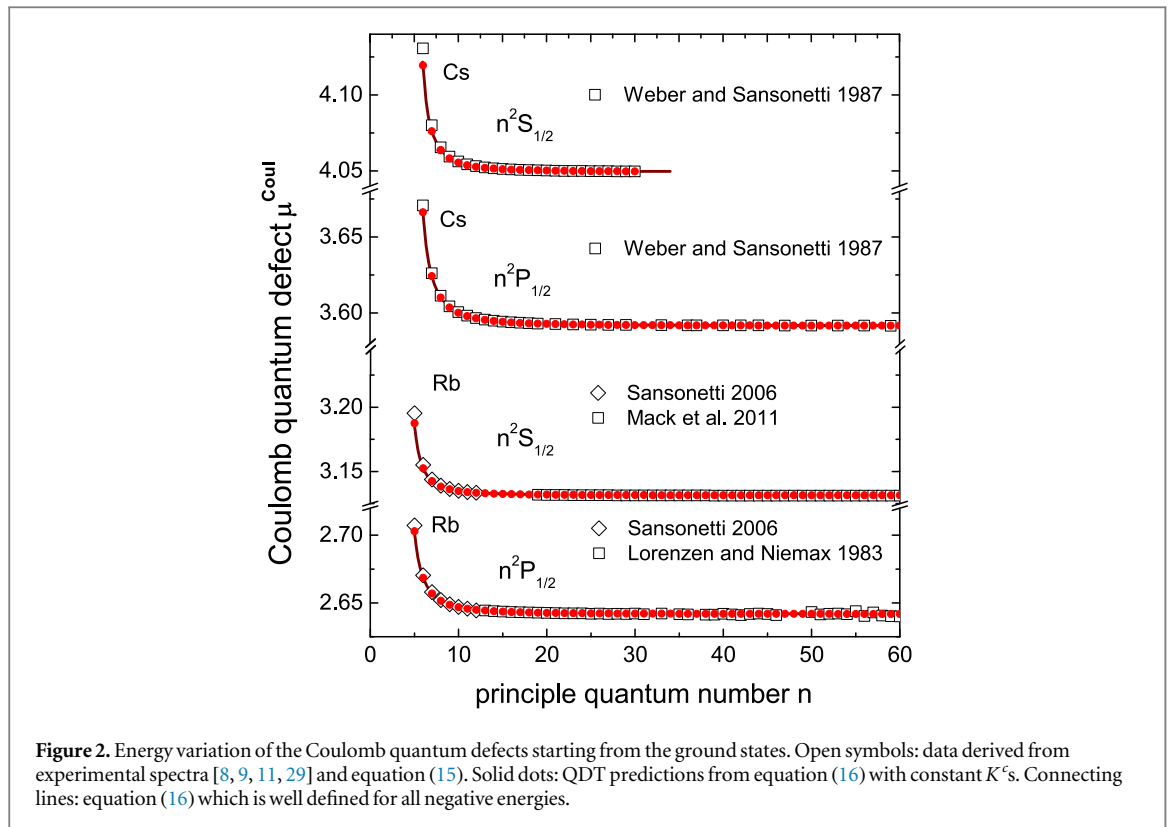
Figure 2. Energy variation of the Coulomb quantum defects starting from the ground states. Open symbols: data derived from experimental spectra [8, 9, 11, 29] and equation (15). Solid dots: QDT predictions from equation (16) with constant K^cs. Connecting lines: equation (16) which is well defined for all negative energies.

makes the centrifugal energy comparable to other electronic energies. The *j* dependence is a reflection of the relativistic effects. Through the *j* dependence of the quantum defect, which can be determined accurately from experimental data, our QDT provides an efficient, yet accurate method for incorporating relativistic effects without solving relativistic equations. It takes full advantage of the fact that relativity is only important close to the nucleus where the electron can potentially move much faster.

4. Discussions and conclusions

The weak energy dependence of K^c (or μ^c), and the degree to which a constant K^c (or μ^c) describes the energy dependence of μ_{lj}^{Coul} show that atomic spectra follow the universal behavior as characterized by the $-C_1/r - C_4/r^4$ solution, not only for high partial wave states [14, 15], but also for the *S* and *P* states, and not only for highly excited states, but also for the first few excited states and the ground state. The weak energy dependence of K^c also implies that the probability for finding this outer electron in the region where the potential defers substantially from $-C_1/r - C_4/r^4$ is small [32], and the wave function, including its normalization, is accurately given by the analytic $-C_1/r - C_4/r^4$ wave function. This combination of spectrum and wave function both following a broader universal behavior is what will lead to the broader universal behaviors in atomic polarizability and the C_6 coefficient for different atoms and different electronic states.

Through the weak energy dependence of its short-range parameters, the two-scale QDT allows the determination of the Rydberg spectra from the measurement of the first few excited states, and allows the spectral determination of the core polarizability [27]. Above the ionization threshold, the theory will provide an analytic description of electron-ion scattering [3, 5, 7] over a wide range of energies. Higher accuracy on the spectra and other atomic properties, when desired, can be achieved by taking into account the weak energy dependence K^c (or μ^c) using a standard Taylor expansion (since they are analytic functions of energy, unlike μ^{Coul} in the presence of the polarization potential). Multichannel [3, 5, 33] and anisotropic generalizations of the theory will extend its description to atomic species other than group-I atoms. The two-scale QDT can also be used in a fully *ab initio* fashion together with a *R*-matrix theory [5, 7], leading to more efficient and accurate calculations with a smaller *R*-matrix box.

In conclusion, we have presented a two-scale QDT for a Coulomb plus polarization potential, and have used it to establish a broader universality in atomic spectra, covering not only the Rydberg states, but also lower lying states including the ground state. Mathematically, the same $-C_1/r - C_4/r^4$ solution is applicable not only to electron-ion, but also to ion-ion interactions. Finally, this first establishment of analytic multiscale QDT gives

hope that similar theories can be developed for other interactions, such as atom–atom [34] and ion–atom [23–25, 35], that are currently treated either at only a single scale [26, 33], or at multiscale but only numerically (see, e.g., [36–38]). If successful, such developments will have impact on almost every aspect of atomic and molecular structure, interactions, and reactions.

Acknowledgments

Appendix. Characteristic exponent for the Coulomb plus polarization potential

The characteristic exponent, ν, as its name implies, plays a central role in the theory of Mathieu class of functions [39], where the concept was first introduced. It came into the Schrödinger equation first through the solutions for the $1/r^4$ potential, which are given in terms of the modified Mathieu functions (see, e.g., [21, 25]). In the more general context of Schrödinger equations, the concept of characteristic exponent is turning out to be a general feature for equations with two essential singularities, one at $r = 0$ and one at $r = \infty$ [26]. It emerged naturally in other single scale solutions for $1/r^6$ [19] and $1/r^3$ [20] potentials, and is appearing again in this first two-scale solution for the $-C_1/r - C_4/r^4$ potential. Mathematically, the characteristic exponent characterizes, for the Schrödinger type of equations, the nature of nonanalytic behavior at the two essential singularities, $r = 0$ and $r = \infty$. Physically, through the factor such as the $|\epsilon_s|^\nu$ in equation (14), it characterizes the nonanalytic behavior of the QDT functions at the threshold $\epsilon_s = 0$. For the $-1/r^6$ potential, for instance, the deviation of ν from its zero-energy value of ν_0 is closely related to the breakdown of the effective range expansion [40].

For the $-C_1/r - C_4/r^4$ potential under investigation here, we have shown that, similar to other $1/r^n$ ($n > 2$) potentials [25, 32], the characteristic exponent ν can be determined either as a root of a characteristic function, or as the root of a Hill determinant [41, 42]. The characteristic function is given by

$$\Lambda_l(\nu, \epsilon_s, \beta_4/\beta_1) := (\nu^2 - \nu_0^2) - \frac{(\beta_4/\beta_1)^2}{\nu}[\bar{Q}(\nu) - \bar{Q}(-\nu)], \tag{18}$$

where $\bar{Q}(\nu)$ is defined in terms of the $Q(\nu)$ function (equation (13)) by

$$\bar{Q}(\nu) = \frac{(\nu + 1/2)^2\epsilon_s + 1/4}{(\nu + 1)[(\nu + 1)^2 - \nu_0^2]}Q(\nu). \tag{19}$$

The Hill determinant is related to the characteristic function and is given by

$$\mathcal{D}_l^H(\nu, \epsilon_s, \beta_4/\beta_1) = \frac{1}{(\nu^2 - \nu_0^2)C_l(\nu)C_l(-\nu)}\Lambda_l(\nu, \epsilon_s, \beta_4/\beta_1), \tag{20}$$

where $C_l(\nu) := \prod_{j=0}^{\infty} Q(\nu + j)$. Defining $\mathcal{H}_l(\epsilon_s, \beta_4/\beta_1) := \mathcal{D}_l^H(\nu = 0, \epsilon_s, \beta_4/\beta_1)$, the ν, as a function of the scaled energy ϵ_s and the length scale ratio β_4/β_1, can be found as the solutions of

$$\cos(2\pi\nu) = 1 - 2\mathcal{H}_l. \tag{21}$$

For $0 \leqslant \mathcal{H}_l \leqslant 1$, ν is real and is given by

$$\nu = l + \frac{1}{2\pi}\cos^{-1}(1 - 2\mathcal{H}_l). \tag{22}$$

For $\mathcal{H}_l < 0$ or $\mathcal{H}_l > 1$, $\nu = \nu_r + i\nu_i$ is complex, with its imaginary part ν_i given by

$$\nu_i = \frac{1}{2\pi}\cosh^{-1}(|1 - 2\mathcal{H}_l|), \tag{23}$$

$$= \frac{1}{2\pi}\ln[|1 - 2\mathcal{H}_l| + \sqrt{(1 - 2\mathcal{H}_l)^2 - 1}]. \tag{24}$$

Its real part is given by

$$\nu_r = \begin{cases} l, & \mathcal{H}_l < 0 \\ l + 1/2, & \mathcal{H}_l > 1 \end{cases}. \tag{25}$$

The real part of ν is defined within a range of 1. All $\nu + j$, where j is an integer, are equivalent.
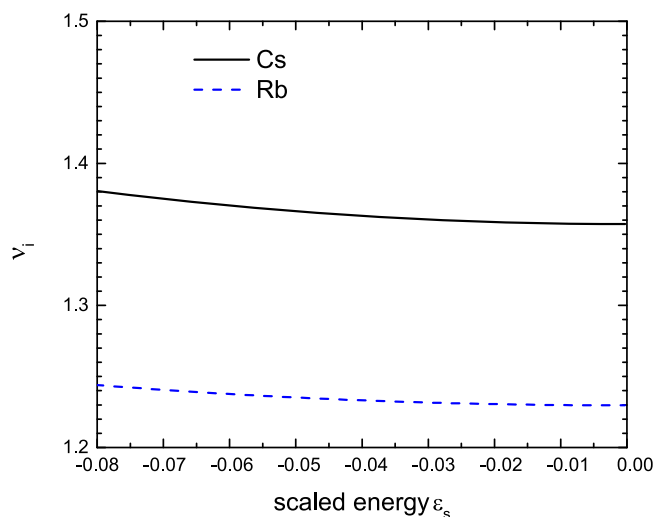
Figure A1. The imaginary part of the *s* wave ($l = 0$) characteristic exponent, ν_i, for Cs and Rb atoms over the range of energies corresponding to that of figure 1. $\nu_r = 0$ over the same range. The exponent is different for different atoms due to their different β_4/β_1. A Mathematica notebook for implementing the QDT functions presented in this work can be found in the Supplementary Data.

As an example, for the *s* wave ($l = 0$) of Cs and Rb atoms in the range of energies corresponding to that of figure 1, the real part of their ν's are equal to zero, and their imaginary parts are functions of energy as illustrated in figure A1. More details of the $-C_1/r - C_4/r^4$ solutions will be presented elsewhere. A Mathematica notebook for implementing the QDT functions presented in this work can be found in the Supplementary Data.

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