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Effective-potential model for high-L Rydberg atoms

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A description of fine-structure patterns in nonpenetrating high-L Rydberg atoms and ions is derived in a perturbative model in which the energy denominators occurring in the second-order perturbation theory are evaluated using the adiabatic expansion. The patterns of Rydberg energies that result are dominated by the expectation value of an effective potential containing a range of tensor orders and increasing negative powers of the Rydberg electron's radial coordinate. The coefficients of each term in the effective potential are expressed in terms of matrix elements and energies of the free ion at the core of the Rydberg system. Smaller corrections to these patterns due to application of the effective potential in second order and due to relativistic and spin contributions are also described. The effective potential provides a framework for extracting ion properties from measurements of high-L fine-structure patterns.

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I. INTRODUCTION

The wave functions and energies of a single Rydberg electron bound to an atomic ion approach purely hydrogenic values as the angular momentum of the Rydberg electron increases. Since the inner classical turning point of the Rydberg electron's radial motion is greater than

$$r_{\mathrm{ITP}} \geqslant \frac{L(L+1)}{2Q}, \tag{1}$$

where L is its angular momentum and Q is the net charge of the core ion, Rydberg electrons of sufficiently high L are effectively confined outside of the region of space occupied by the ion core. Their interactions with the ion core are dominated by the fully screened Coulomb attraction that binds them in their orbit. Any additional interactions are weak and long-ranged. In the absence of these additional interactions, all high-L Rydberg levels of the same principal quantum number would be degenerate except for small relativistic effects. The presence of the weak long-range interactions lifts this degeneracy and produces a pattern of binding energies that reflects the strength and character of these interactions. Measurement of these "fine-structure patterns" is therefore a convenient probe of the core properties that control the strength of the long-range interactions, such as polarizabilities and permanent electric moments. Many of these properties are very difficult to measure for neutral atoms, and consequently the ion properties extracted from high-L Rydberg spectroscopy represent a unique probe of atomic structure theory.

The complexity of these fine-structure patterns depends directly on the angular momentum of the core ion, J_c. These patterns represent an example of "pair coupling" where the spin of the Rydberg electron is nearly negligible and the intermediate angular momentum,

$$\vec{K} = \vec{J}_c + \vec{L}, \tag{2}$$

describes the eigenstates [1]. In general, there are $2J_c + 1$ energies possible for each value of the Rydberg electron's orbital angular momentum, L. Consequently, in what follows, K will be considered to be the total angular momentum of the Rydberg system, and the small effect of the Rydberg electron's spin will be treated separately.

The basic idea of using the spectroscopy of nonpenetrating Rydberg levels to extract information about the properties of the ion core was discussed very early by Mayer and Mayer in 1933 [2]. In the case of Rydberg atoms or ions with S-state cores, the deviation of the term energies from their hydrogenic values was related to the dipole and quadrupole polarizabilities of the ion with a model considering the electric field and field gradient produced by a stationary Rydberg electron. This led to a simple expression for the energy change in terms of the expectation value of an effective potential:

$$\Delta E = \left\langle -\frac{1}{2}\frac{\alpha_D}{r^4} - \frac{1}{2}\frac{\alpha_Q}{r^6} \right\rangle_{nL}. \tag{3}$$

The two basic assumptions underlying this approach are common to all treatments of high-L Rydberg structure, including the following report.

(A1) The Rydberg electron is distinguishable from the electrons in the ion core.

(A2) The Rydberg electron is always farther from the nucleus than any of the core electrons.

In addition, this early approximation neglects the dynamics of the Rydberg electron, effectively assuming that the core adjusts adiabatically to the motion of the Rydberg electron. A number of approaches were later advanced to incorporate corrections to this adiabatic model [3–5]. If the corrections to the adiabatic picture are small, Kleinman, Hahn, and Spruch showed that adding a term proportional to r^{-6} to the potential could account approximately for the nonadiabatic effects [5]:

$$\alpha_Q \Rightarrow (\alpha_Q - 6\beta_D), \tag{4}$$

where β_D was an additional core property often referred to as the "nonadiabatic dipole polarizability."

A major step in the further development of the effective potential model for high-L Rydberg structure was the treatment of Rydberg levels of helium by Drachman [6–8]. In a sequence of papers, he systematically derived an effective potential for helium Rydberg electrons that contained additional terms proportional to higher inverse powers of the Rydberg radial coordinate up to r^{-10}. The dynamics of the Rydberg electron were found to lead to significant deviations from the adiabatic model, and these were systematically included. Since the core ion in this case was He$^+$, whose nonrelativistic wave functions were known, all the coefficients occurring in the effective potential were calculated analytically. Although Drachman used the Feshbach projection operator technique to organize his calculation, in essence it consisted of systematically applying the following three expansions.

(i) Static perturbation theory.
(ii) Multipole expansion of the perturbing term.
(iii) A power-series expansion of the energy denominators occurring in (i), described fully below, which we refer to as the "adiabatic expansion" because the leading term corresponds to the adiabatic model.

Because the zeroth-order wave functions of the Rydberg electron satisfy the hydrogenic radial equation, it was possible to manipulate the resulting expressions into a form where successive terms were proportional to increasing negative powers of r, yielding the effective potential. The expectation value of each term could be evaluated using standard expressions for the radial expectation values of hydrogenic functions. In the case of helium Rydberg levels, the results of this approach were confirmed with completely independent variational calculations [9] and with precise experimental measurements [10,11]. The precision of the predictions obtained with the effective potential method is limited by the convergence of the asymptotic series of terms, but this approach has the great advantage that it can be applied to any Rydberg level, (n,L), without the necessity of a specific calculation for that state's wave function. The variational method is much more computationally intensive.

The calculation presented here is modeled after the work of Drachman. Its key feature is use of the adiabatic expansion and manipulation of the perturbation expressions using the hydrogenic radial equation satisfied by the zeroth-order Rydberg electron wave function. However, the present calculation extends the work of Drachman in two significant ways. First, the core properties that occur in the effective potential are expressed as functions of the matrix elements and energies of the core ion instead of being evaluated analytically as was possible for the He$^+$ core. Second, the angular momentum of the core ion, J_c, is not restricted. This gives rise to higher rank tensor operators not present in the helium case. Taken together, these extensions make the results applicable to a wide range of Rydberg systems. Some of the terms derived here are well known, such as the terms in Eq. (3) and the related tensor polarization terms. Others are new. Many of the higher-order terms occur in a related treatment of Rydberg electrons bound to anisotropic core ions, treated in a coupled-channel approach by Clark, Greene, and Miecznik [12]. The approach presented here differs from that calculation in several ways. The main difference is that this report, based on a perturbation expansion, calculates only the differences from the known zeroth-order Rydberg energies. In contrast, the approach of Clark, Greene, and Miecznik depends on a specific calculation of the radial function and full energy eigenvalue for each level in the appropriate channel potential. Another difference between the calculations is in the method of including corrections to the adiabatic approximation. The effective potential model presented here has the advantage that it is easily applied to describe a wide range of high-L Rydberg systems without the need for extensive calculations.

II. DERIVATION

For simplicity, we assume initially a completely nonrelativistic system of N electrons, bound to a nucleus of charge Z. Using assumption (A1) above, the Nth electron is taken to be the distinguishable Rydberg electron, and the Hamiltonian is written in a form that makes that distinction. The zeroth-order Hamiltonian is the sum of a Hamiltonian describing the free ion and a Hamiltonian describing a hydrogenic Rydberg electron bound by the net charge of the core ion. Everything left over from the full nonrelativistic Hamiltonian represents the perturbation V,

$$H = \left(H^0_{\text{core}} + H^0_{\text{Ryd}}\right) + V, \tag{5}$$

where

$$H^0_{\text{core}} = \sum_{i=1}^{N-1}\left(\frac{|\vec{p}_i|^2}{2} - \frac{Z}{r_i}\right) + \sum_{\substack{i=1\\ j>i}}^{N-1}\frac{1}{r_{ij}}, \tag{6}$$

$$H^0_{\text{Ryd}} = \frac{|\vec{p}_N|^2}{2} - \frac{Q}{r_N}, \tag{7}$$

and

$$V = \sum_{i=1}^{N-1}\frac{1}{r_{iN}} - \frac{(N-1)}{r_N}, \tag{8}$$

and where Z is the nuclear charge, $Q = Z - N + 1$ is the charge of the ion core, and $N-1$ is the number of electrons within the ion core. The further assumption (A2) allows the potential to be written as a multipole expansion with no scalar (i.e., $\kappa = 0$) term:

$$V = \sum_{\kappa=1}^{\infty}\sum_{i=1}^{N-1} r_i^{\kappa} C^{[\kappa]}(\hat{r}_i)\cdot\frac{C^{[\kappa]}(\hat{r}_N)}{r_N^{\kappa+1}} = \sum_{\kappa=1}^{\infty} M^{[\kappa]}\cdot\frac{C^{[\kappa]}(\hat{r}_N)}{r_N^{\kappa+1}}, \tag{9}$$

where

$$M^{[\kappa]} = \sum_{i=1}^{N-1} r_i^{\kappa} C^{[\kappa]}(\hat{r}_i). \tag{10}$$

The operators $M^{[\kappa]}$ with $\kappa = 1,2,3,4$ represent the dipole, quadrupole, octupole, and hexadecapole moment operators acting on the core ion wave function. At this point, the subscript on r_N may be dropped since the positions of the core electrons are not explicitly mentioned again.

The zeroth-order wave functions are written as products of the form

$$|\Psi^0\rangle = \left|\Psi^0_{\text{core}}\right\rangle\left|\Psi^0_{\text{Ryd}}\right\rangle,$$

where $|\Psi^0_{\text{core}}\rangle$ is the wave function of the free ion core and $|\Psi^0_{\text{Ryd}}\rangle$ is the hydrogenic wave function of the Rydberg electron. We assume that the core functions are eigenstates of parity, angular momentum, and H^0_{core}. They are denoted by $|\lambda,J_c,m_J\rangle$, where λ stands for any additional quantum numbers required to specify a particular state. These functions, of course, are known only in the abstract. The Rydberg functions are specified by $|n,L,m\rangle$ and are the well-known hydrogenic wave functions corresponding to a core charge of Q and a reduced mass $\mu = m_e m_c/(m_e + m_c)$. Ignoring the spin of the electron, these wave functions couple together to form the angular momentum K:

$$\vec{K} = \vec{L} + \vec{J}_C,$$

where K ranges from $|\vec{L} - \vec{J}_C|$ to $|\vec{L} + \vec{J}_C|$. In general, we denote an arbitrary state of the combined system as $|\lambda' J_c', nL; K\rangle$. We seek to describe the energies of Rydberg levels that correspond in zeroth order to states in which the core is in its ground state, denoted as $|gJ_c\rangle$, the Rydberg electron is in the (n,L) level, and the total angular momentum, exclusive of Rydberg spin, is K. We denote these as $|gJ_c,nL;K\rangle$, or by the shorthand notation $|nL_K\rangle$.

A. Zeroth- and first-order energies

Applying static perturbation theory, the energy of the nL_K state is given by

$$E(nL_K) = E^{[0]} + E^{[1]} + E^{[2]} + \cdots. \tag{11}$$

The zeroth-order energy is the sum of that of a free ion and a hydrogenic electron:

$$E^{[0]}(n) = E(gJ_c) - \frac{1}{2}\frac{m_c}{(m_c + m_e)}\frac{Q^2}{n^2}, \tag{12}$$

where m_c is the core mass and m_e is the electron mass.

The first-order energy perturbation energies come from the permanent electric moments of the core ion. There are no odd permanent moments because of parity constraints. An ion core with angular momentum of $J_c \geqslant 1$, however, may have a quadrupole moment, while a nonzero hexadecapole moment is possible if $J_c \geqslant 2$:

$$\begin{aligned} E^{[1]}(nL_K) &= \Big\langle gJ_c,nL;K\Big|\sum_{\kappa=1}^{\infty} M^{[\kappa]}\cdot\frac{C^{[\kappa]}(\hat{r})}{r^{\kappa+1}}\Big|gJ_c,nL;K\Big\rangle \\ &= -Q\langle r^{-3}\rangle_{nL}\frac{\langle X^{[2]}(J_c)\cdot C^{[2]}(\hat{r})\rangle}{\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c\end{pmatrix}} - \Pi\langle r^{-5}\rangle_{nL} \\ &\quad\times\frac{\langle X^{[4]}(J_c)\cdot C^{[4]}(\hat{r})\rangle}{\begin{pmatrix} J_c & 4 & J_c \\ -J_c & 0 & J_c\end{pmatrix}} + \cdots, \end{aligned} \tag{13}$$

where

$$Q \equiv -\big\langle gJ_c,m_J = J_c\big|M_0^{[2]}\big|gJ_c,m_J = J_c\big\rangle \tag{14}$$

is the core's electric quadrupole moment, and

$$\Pi \equiv -\big\langle gJ_c,m_J = J_c\big|M_0^{[4]}\big|gJ_c,m_J = J_c\big\rangle \tag{15}$$

is the core's electric hexadecapole moment. $X^{[b]}(J_c)$ is a unit bth rank tensor in the space of the ion core, while $C^{[b]}(\hat{r})$ is a spherical bth rank tensor in the Rydberg electron's angular position. The next possible permanent moment, of order $\kappa = 6$, requires $J_c \geqslant 3$.

B. Second-order energy (core excited intermediate states)

Equation (16) shows the general expression for the second-order energies:

$$E^{[2]}(nL_K) = \sum_{\lambda',J_c',n',L'} \frac{\big\langle gJ_c,nL;K\big|\sum_{\kappa_1=1}^{\infty} M^{[\kappa_1]}\cdot\frac{C^{[\kappa_1]}(\hat{r})}{r^{\kappa_1+1}}\big|\lambda' J_c',n'L';K\big\rangle\big\langle\lambda' J_c',n'L';K\big|\sum_{\kappa_2=1}^{\infty} M^{[\kappa_2]}\cdot\frac{C^{[\kappa_2]}(\hat{r})}{r^{\kappa_2+1}}\big|gJ_c,nL;K\big\rangle}{[E(gJ_c) + E(n)] - [E(\lambda' J_c') + E(n')]}. \tag{16}$$

We initially consider only the portion of the total second-order energy that is due to intermediate states where the core is electronically excited. This excludes intermediate states where the core is in its ground electronic state, either the true ground state or an excited fine-structure level of the ground electronic state. The total second-order energy is the sum of terms consisting of the various multipole orders occurring in the potential V,

$$E^{[2]}(nL_K) = \sum_{\kappa_1,\kappa_2} E^{[2]}(\kappa_1,\kappa_2).$$

Using the methods of Ref. [13], the core and Rydberg electron parts of the matrix elements may be factored and the partial contribution due to specific multipole terms κ_1 and κ_2 written as

$$E^{[2]}(\kappa_1,\kappa_2) = -\sum_{\lambda',J_c',n',L'}\left[(-1)^{J_c'-J_c}\begin{Bmatrix} K & L & J_c \\ \kappa_1 & J_c' & L' \end{Bmatrix}\begin{Bmatrix} K & L' & J_c' \\ \kappa_2 & J_c & L \end{Bmatrix}\begin{pmatrix} L & \kappa_1 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L' & \kappa_2 & L \\ 0 & 0 & 0 \end{pmatrix}(2L+1)(2L'+1)\right.$$
$$\left.\times\frac{\langle gJ_c\|M^{[\kappa_1]}\|\lambda' J_c'\rangle\langle\lambda' J_c'\|M^{[\kappa_2]}\|gJ_c\rangle[nL|r^{-(\kappa_1+1)}|n'L'][n'L'|r^{-(\kappa_2+1)}|nL]}{\Delta E(\lambda' J_c') + E(n') - E(n)}\right], \tag{17}$$

where

$$\Delta E(\lambda' J_c') = E(\lambda' J_c') - E(gJ_c).$$

As Eq. (17) indicates, only multipole terms with $\kappa_1 + \kappa_2$ even can contribute to $E^{[2]}$.

Further simplification of this expression relies upon the "adiabatic expansion." This expansion is based on the assumption that the energy difference in the denominator is primarily due to the core energy difference, allowing the denominator to be expanded as

$$\frac{1}{\Delta E(\lambda' J_c') + E(n') - E(n)} = \frac{1}{\Delta E(\lambda' J_c')} - \frac{[E(n') - E(n)]}{[\Delta E(\lambda' J_c')]^2} + \frac{[E(n') - E(n)]^2}{[\Delta E(\lambda' J_c')]^3} + \cdots. \tag{18}$$

If it is valid, the adiabatic expansion allows the sums over n' to be carried out explicitly using the properties of hydrogenic radial functions. The leading term, for instance, corresponds to the adiabatic approximation where the dynamics of the Rydberg electron are neglected. When this is substituted into Eq. (17), the only dependence on n' is in the radial matrix elements and the completeness of the radial functions for fixed L' allows the summation over n' to be carried out:

$$\sum_{n'}\langle nL|r^{-s}|n'L'\rangle\langle n'L'|r^{-q}|nL\rangle = \langle r^{-(s+q)}\rangle_{nL}. \tag{19}$$

Note that in this and similar sums, the sum over n' includes continuum levels of the same L'. This leads to expressions, described below, for all the adiabatic terms in the effective potential.

The second term in the adiabatic expansion also leads to expressions that can be simplified using properties of the Rydberg radial functions. Making use of the radial wave equation satisfied by hydrogenic functions, and using repeated application of integration by parts, it can be shown that

$$\sum_{n'}[E(n') - E(n)]\langle nL|r^{-s}|n'L'\rangle\langle n'L'|r^{-q}|nL\rangle = \frac{1}{2}[sq - L(L+1) + L'(L'+1)]\langle r^{-(s+q+2)}\rangle_{nL}. \tag{20}$$

This leads to a sequence of terms, detailed below, which we refer to as the first nonadiabatic terms.

The expressions obtained by substituting the third term of the adiabatic expansion into Eq. (17) can also be simplified. Using the radial equation satisfied by the Rydberg radial functions, it can be shown that [14]

$$\begin{aligned}&\sum_{n'}[E(n') - E(n)]^2\langle nL|r^{-s}|n'L'\rangle\langle n'L'|r^{-q}|nL\rangle\\
&\quad= -\frac{sq}{s+q+1}(Q\langle r^{-(s+q+3)}\rangle_{nL} - L(L+1)\langle r^{-(s+q+4)}\rangle_{nL})\\
&\qquad+\frac{1}{4}(s+q)(s+q+3)[-L(L+1) + L'(L'+1)]\langle r^{-(s+q+4)}\rangle_{nL}\\
&\qquad+\frac{1}{4}[-s(s+1) - L(L+1) + L'(L'+1)][-q(q+1) - L(L+1) + L'(L'+1)]\langle r^{-(s+q+4)}\rangle_{nL}.\end{aligned} \tag{21}$$

We refer to the resulting additional terms in the effective potential as the second nonadiabatic terms.

The second-order energy for a particular κ_1 and κ_2 may thus be written as an adiabatic term,

$$E^{[2]}(\kappa_1,\kappa_2)_{\mathrm{AD}} = -\sum_{\lambda',J_c',L'}\left[(-1)^{J_c'-J_c}\begin{Bmatrix} K & L & J_c \\ \kappa_1 & J_c' & L' \end{Bmatrix}\begin{Bmatrix} K & L' & J_c' \\ \kappa_2 & J_c & L \end{Bmatrix}\begin{pmatrix} L & \kappa_1 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L' & \kappa_2 & L \\ 0 & 0 & 0 \end{pmatrix}(2L+1)(2L'+1)\right.$$
$$\left.\times\frac{\langle gJ_c\|M^{[\kappa_1]}\|\lambda' J_c'\rangle\langle\lambda' J_c'\|M^{[\kappa_2]}\|gJ_c\rangle}{\Delta E(\lambda' J_c')}\langle r^{-(\kappa_1+\kappa_2+2)}\rangle_{nL}\right], \tag{22}$$

a first nonadiabatic term,

$$E^{[2]}(\kappa_1,\kappa_2)_{\mathrm{1st\,NA}} = -\sum_{\lambda',J_c',L'}\Bigg[(-1)^{J_c'-J_c}\begin{Bmatrix} K & L & J_c \\ \kappa_1 & J_c' & L' \end{Bmatrix}\begin{Bmatrix} K & L' & J_c' \\ \kappa_2 & J_c & L \end{Bmatrix}\begin{pmatrix} L & \kappa_1 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L' & \kappa_2 & L \\ 0 & 0 & 0 \end{pmatrix}(2L+1)(2L'+1)$$
$$\times\frac{\langle gJ_c\|M^{[\kappa_1]}\|\lambda'J_c'\rangle\langle\lambda'J_c'\|M^{[\kappa_2]}\|gJ_c\rangle}{[\Delta E(\lambda'J_c')]^2}\left(-\frac{1}{2}[(\kappa_1+1)(\kappa_2+1)-L(L+1)+L'(L'+1)]\right)\langle r^{-(\kappa_1+\kappa_2+4)}\rangle_{nL}\Bigg], \tag{23}$$

and a second nonadiabatic term,

$$E^{[2]}(\kappa_1,\kappa_2)_{\mathrm{2nd\,NA}} = -\sum_{\lambda',J_c',L'}\Bigg[(-1)^{J_c'-J_c}\begin{Bmatrix} K & L & J_c \\ \kappa_1 & J_c' & L' \end{Bmatrix}\begin{Bmatrix} K & L' & J_c' \\ \kappa_2 & J_c & L \end{Bmatrix}\begin{pmatrix} L & \kappa_1 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L' & \kappa_2 & L \\ 0 & 0 & 0 \end{pmatrix}(2L+1)(2L'+1)$$
$$\times\frac{\langle gJ_c\|M^{[\kappa_1]}\|\lambda'J_c'\rangle\langle\lambda'J_c'\|M^{[\kappa_2]}\|gJ_c\rangle}{[\Delta E(\lambda'J_c')]^3}\Bigg(-\frac{(\kappa_1+1)(\kappa_2+1)}{\kappa_1+\kappa_2+3}Q\langle r^{-(\kappa_1+\kappa_2+5)}\rangle_{nL}+\Bigg(\frac{(\kappa_1+1)(\kappa_2+1)}{\kappa_1+\kappa_2+3}L(L+1)$$
$$+\frac{1}{4}(\kappa_1+\kappa_2+2)(\kappa_1+\kappa_2+5)[-L(L+1)+L'(L'+1)]+\frac{1}{4}[-(\kappa_1+1)(\kappa_1+2)-L(L+1)$$
$$+L'(L'+1)][-(\kappa_2+1)(\kappa_2+2)-L(L+1)+L'(L'+1)]\Bigg)\langle r^{-(\kappa_1+\kappa_2+6)}\rangle_{nL}\Bigg)\Bigg]. \tag{24}$$

Taken together this gives a total second-order energy, from electronically excited core levels, of

$$E^{[2]}(nL_K) = \sum_{\kappa_1,\kappa_2}[E^{[2]}(\kappa_1,\kappa_2)_{\mathrm{AD}} + E^{[2]}(\kappa_1,\kappa_2)_{\mathrm{1st\,NA}} + E^{[2]}(\kappa_1,\kappa_2)_{\mathrm{2nd\,NA}}]. \tag{25}$$

Note that each successive term in the adiabatic expansion is proportional to higher inverse powers of the Rydberg radial coordinate.

The contributions to the second-order perturbation energy from a fixed multipole order (κ_1, κ_2) and adiabatic order (AD, 1st NA, 2nd NA) can each be decomposed into contributions of different tensor orders. This decomposition is most easily accomplished by noting that the entire dependence on K is contained in the product of two $6J$ symbols that occurs in each of the expressions above. The $(2J_c + 1)$-dimensional space corresponding to the different values of K for a common L is spanned by the basis vectors,

$$V_b(K) = (-1)^{J_c+L+K}\begin{Bmatrix} K & L & J_c \\ b & J_c & L \end{Bmatrix}\sqrt{2b+1}\quad (b = 0,1,2,\ldots), \tag{26}$$

which satisfy

$$\sum_K (2K+1)V_b(K)V_{b'}(K) = \delta_{bb'}. \tag{27}$$

The $6J$-symbol products that occur in the energy expressions may be written as linear combinations of these basis vectors using Eq. (6.2.12) of Ref. [13],

$$\begin{Bmatrix} K & L & J_c \\ \kappa_1 & J_c' & L' \end{Bmatrix}\begin{Bmatrix} K & L' & J_c' \\ \kappa_2 & J_c & L \end{Bmatrix} = \sum_{b=0}^{\infty} a_b(J_c',L')V_b(K), \tag{28}$$

where

$$a_b(J_c',L') = \left[(-1)^{L+L'}\begin{Bmatrix} L' & \kappa_1 & L \\ b & L & \kappa_2 \end{Bmatrix}\right]\left[(-1)^{J_c+J_c'}\begin{Bmatrix} J_c' & \kappa_1 & J_c \\ b & J_c & \kappa_2 \end{Bmatrix}\right][(-1)^b\sqrt{2b+1}]. \tag{29}$$

Notice that this substitution factors the dependence on L' and J_c'. Notice also that the $6J$ symbols restrict the possible tensor orders, b, to between $|\kappa_1 - \kappa_2|$ and $|\kappa_1 + \kappa_2|$, with an upper limit of the smaller of $2L$ and $2J_c$.

Substituting this result into the energy expressions allows each to be written as a sum of tensor orders:

$$E^{[2]}(nL_K) = \sum_b E_b^{[2]}(nL_K), \tag{30}$$

where

$$E_b^{[2]}(nL_K) = \sum_{\kappa_1,\kappa_2} E_b^{[2]}(\kappa_1,\kappa_2)_{\mathrm{AD}} + E_b^{[2]}(\kappa_1,\kappa_2)_{\mathrm{1st\,NA}} + E_b^{[2]}(\kappa_1,\kappa_2)_{\mathrm{2nd\,NA}}. \tag{31}$$

Since the resulting expressions separate the terms involving L', the sum over L' may be evaluated term by term. The result is a sequence of terms of increasing negative powers of r for each tensor order whose coefficients are functions of the matrix elements and energies of the excited core levels.

The resulting scalar terms ($b = 0$) are

$$E_0^{[2]}(nL_K) = -\frac{1}{2}\Bigg(\alpha_{D,0}\langle r^{-4}\rangle_{nL} + (\alpha_{Q,0} - 6\beta_{D,0})\langle r^{-6}\rangle_{nL} - \frac{16Q}{5}\gamma_{D,0}\langle r^{-7}\rangle_{nL} + \left(\alpha_{O,0} - 6\beta_{Q,0} + 72\gamma_{D,0}\left(1 + \frac{L(L+1)}{10}\right)\right)\langle r^{-8}\rangle_{nL}\Bigg), \tag{32}$$

where the coefficients in front of the core parameters follow the convention of Ref. [6]. The core parameters are given by

$$\alpha_{D,0} = \frac{2}{3}\frac{1}{2J_c+1}\sum_{\lambda',J_c'}\frac{\langle gJ_c\|M^{[1]}\|\lambda'J_c'\rangle^2}{\Delta E(\lambda'J_c')}, \tag{33}$$

$$\alpha_{Q,0} = \frac{2}{5}\frac{1}{2J_c+1}\sum_{\lambda',J_c'}\frac{\langle gJ_c\|M^{[2]}\|\lambda'J_c'\rangle^2}{\Delta E(\lambda'J_c')}, \tag{34}$$

$$\alpha_{O,0} = \frac{2}{7}\frac{1}{2J_c+1}\sum_{\lambda',J_c'}\frac{\langle gJ_c\|M^{[3]}\|\lambda'J_c'\rangle^2}{\Delta E(\lambda'J_c')}, \tag{35}$$

$$\beta_{D,0} = \frac{1}{3}\frac{1}{2J_c+1}\sum_{\lambda',J_c'}\frac{\langle gJ_c\|M^{[1]}\|\lambda'J_c'\rangle^2}{[\Delta E(\lambda'J_c')]^2}, \tag{36}$$

$$\beta_{Q,0} = \frac{1}{2}\frac{J1}{2J_c+1}\sum_{\lambda',J_c'}\frac{\langle gJ_c\|M^{[2]}\|\lambda'J_c'\rangle^2}{[\Delta E(\lambda'J_c')]^2}, \tag{37}$$

and

$$\gamma_{D,0} = \frac{1}{6}\frac{1}{2J_c+1}\sum_{\lambda',J_c'}\frac{\langle gJ_c\|M^{[1]}\|\lambda'J_c'\rangle^2}{[\Delta E(\lambda'J_c')]^3}. \tag{38}$$

Notice that the summed quantities are positive definite, so each of the scalar coefficients is a simple sum of the contributions from the several possible branches characterized by J_c'. The terms proportional to r^{-4} and r^{-6} are well known. The later terms are analogous to those derived by Drachman, but are not restricted to the special case $J_c = 0$. The terms proportional to r^{-4} and r^{-6} agree with the results of Clark, Greene, and Miecznik [12] except that their expression for the coefficient analogous to $\beta_{D,0}$ contains an additional contribution [the second term in their Eq. (28)].

The vector term of the second-order energy ($b = 1$) can be written as

$$E_1^{[2]}(nL_K) = (\beta_{D,1}\langle r^{-6}\rangle_{nL} + (\beta_{Q,1} + \gamma_{D,1})\langle r^{-8}\rangle_{nL})\vec{L}\cdot\vec{J}_c, \tag{39}$$

where the core parameters are defined by

$$\beta_{D,1} = \frac{\sqrt{6}}{\sqrt{2J_c(2J_c+1)(2J_c+2)}}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 1 & J_c \\ 1 & J_c & 1 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda'J_c'\rangle^2}{[\Delta E(\lambda'J_c')]^2}, \tag{40}$$

$$\beta_{Q,1} = -3\sqrt{\frac{6}{5}}\frac{1}{\sqrt{2J_c(2J_c+1)(2J_c+2)}}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 2 & J_c \\ 1 & J_c & 2 \end{Bmatrix}\frac{\langle gJ_c\|M^{[2]}\|\lambda'J_c'\rangle^2}{[\Delta E(\lambda'J_c')]^2}, \tag{41}$$

and

$$\gamma_{D,1} = -9\sqrt{6}\frac{1}{\sqrt{2J_c(2J_c+1)(2J_c+2)}}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 1 & J_c \\ 1 & J_c & 1 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda'J_c'\rangle^2}{[\Delta E(\lambda'J_c')]^3}. \tag{42}$$

In this case, the contributions of the several J_c' branches may either add or subtract from the total coefficient. Notice also that there is no adiabatic vector term. This is due to a cancellation between the contributions of adiabatic terms with different L'. A similar cancellation does not occur in the nonadiabatic terms because of the extra factors of L and L' that occur in Eqs. (20) and (21). The vector term in high-L Rydberg fine structure has an interesting history that is discussed in Sec. III. The existence of a vector term in Rydberg electric fine structure was first predicted by Zygelman [15]. Its coefficient was first calculated by Clarke, Greene, and Miecznik [12], who also emphasized its essentially nonadiabatic nature. Our expression for $\beta_{D,1}$ agrees with their result. The terms proportional to r^{-8} are new. In nature these terms compete with a much larger vector term due to the magnetic dipole moment of the core electron, discussed in Sec. II D. Nevertheless, the electric vector structure has been measured in both argon [16] and neon [17].

For consistency with previous publications and with the leading term from Sec. II A proportional to the quadrupole moment, the $b = 2$ term is written as proportional to

$$\frac{\langle X^{[2]}(J_c)\cdot C^{[2]}(\hat{r})\rangle}{\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}}. \tag{43}$$

This leads to tensor terms of the form

$$\begin{aligned} E_2^{[2]}(nL_K) = -\frac{1}{2}\Bigg(&\alpha_{D,2}\langle r^{-4}\rangle_{nL} + (\alpha_{Q,2} - 6\beta_{D,2} + \alpha_{DO,2})\langle r^{-6}\rangle_{nL} - \frac{16Q}{5}\gamma_{D,2}\langle r^{-7}\rangle_{nL} \\ &+ \left(\alpha_{O,2} - 6\beta_{Q,2} + \alpha_{QH,2} - 6\beta_{DO,2} + 72\left(\frac{L(L+1)}{10} + \frac{1}{4}\right)\gamma_{D,2}\right)\langle r^{-8}\rangle_{nL}\Bigg)\frac{\langle X^{[2]}(J_c)\cdot C^{[2]}(\hat{r})\rangle}{\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}}, \end{aligned} \tag{44}$$

where the core parameters are given by

$$\alpha_{D,2} = 2\sqrt{\frac{10}{3}}\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 1 & J_c \\ 2 & J_c & 1 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda' J_c'\rangle^2}{\Delta E(\lambda' J_c')}, \tag{45}$$

$$\alpha_{Q,2} = -2\sqrt{\frac{10}{7}}\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 2 & J_c \\ 2 & J_c & 2 \end{Bmatrix}\frac{\langle gJ_c\|M^{[2]}\|\lambda' J_c'\rangle^2}{\Delta E(\lambda' J_c')}, \tag{46}$$

$$\alpha_{O,2} = \frac{4}{3}\sqrt{\frac{15}{7}}\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 3 & J_c \\ 2 & J_c & 3 \end{Bmatrix}\frac{\langle gJ_c\|M^{[3]}\|\lambda' J_c'\rangle^2}{\Delta E(\lambda' J_c')}, \tag{47}$$

$$\alpha_{DO,2} = -4\sqrt{\frac{15}{7}}\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{2J_c'}\begin{Bmatrix} J_c' & 1 & J_c \\ 2 & J_c & 3 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda' J_c'\rangle\langle\lambda' J_c'\|M^{[3]}\|gJ_c\rangle}{\Delta E(\lambda' J_c')}, \tag{48}$$

$$\alpha_{QH,2} = 4\sqrt{\frac{10}{7}}\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{2J_c'}\begin{Bmatrix} J_c' & 2 & J_c \\ 2 & J_c & 4 \end{Bmatrix}\frac{\langle gJ_c\|M^{[2]}\|\lambda' J_c'\rangle\langle\lambda' J_c'\|M^{[4]}\|gJ_c\rangle}{\Delta E(\lambda' J_c')}, \tag{49}$$

$$\beta_{D,2} = \frac{1}{2}\sqrt{\frac{10}{3}}\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 1 & J_c \\ 2 & J_c & 1 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda' J_c'\rangle^2}{[\Delta E(\lambda' J_c')]^2}, \tag{50}$$

$$\beta_{Q,2} = -2\sqrt{\frac{10}{7}}\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 2 & J_c \\ 2 & J_c & 2 \end{Bmatrix}\frac{\langle gJ_c\|M^{[2]}\|\lambda' J_c'\rangle^2}{[\Delta E(\lambda' J_c')]^2}, \tag{51}$$

$$\beta_{DO,2} = -4\sqrt{\frac{15}{7}}\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{2J_c'}\begin{Bmatrix} J_c' & 1 & J_c \\ 2 & J_c & 3 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda' J_c'\rangle\langle\lambda' J_c'\|M^{[3]}\|gJ_c\rangle}{[\Delta E(\lambda' J_c')]^2}, \tag{52}$$

$$\gamma_{D,2} = \frac{1}{2}\sqrt{\frac{10}{3}}\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 1 & J_c \\ 2 & J_c & 1 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda' J_c'\rangle^2}{[\Delta E(\lambda' J_c')]^3}. \tag{53}$$

The term proportional to r^{-4} is standard, and the expression for $\alpha_{D,2}$ agrees with that first described by Angel and Sandars [18]. The terms proportional to r^{-6} agree with the results of Clark, Greene, and Miecznik [12], except for an additional term that is included in their Eq. (29). The additional terms are new.

The portion of $E^{[2]}$ proportional to the scalar product of third rank tensors is initially found as a multiple of $V_3(K)$:

$$V_3(K) = \sqrt{7}\langle X^{[3]}(J_c)\cdot X^{[3]}(\hat{r})\rangle, \tag{54}$$

where $X^{[3]}(J_c)$and $X^{[3]}(\hat{r})$ are unit tensors. Since only matrix elements diagonal in L are desired for this term, it is convenient to write it in terms of a specific third-rank tensor

$$T^{[3]}(\hat{r}) \equiv (C^{[2]}(\hat{r})\otimes\vec{L})^{[3]}, \tag{55}$$

whose reduced matrix elements are given by

$$\langle L|T^{[3]}(\hat{r})|L\rangle = -\frac{1}{4}\sqrt{\frac{3}{5}}\sqrt{\frac{(2L-2)2L(2L+1)(2L+2)(2L+4)}{(2L-1)(2L+3)}}. \tag{56}$$

The resulting contributions to $E^{[2]}$ are

$$E_3^{[2]}(nL_K) = (\beta_{Q,3} + \beta_{DO,3})\langle r^{-8}\rangle_{nL}\langle X^{[3]}(J_c)\cdot T^{[3]}(\hat{r})\rangle, \tag{57}$$

with the core parameters defined as

$$\beta_{Q,3} = \sqrt{\frac{21}{2}}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 2 & J_c \\ 3 & J_c & 2 \end{Bmatrix}\frac{\langle gJ_c\|M^{[2]}\|\lambda' J_c'\rangle^2}{[\Delta E(\lambda' J_c')]^2} \tag{58}$$

and

$$\beta_{DO,3} = \sqrt{35}\sum_{\lambda',J_c'}(-1)^{2J_c'}\begin{Bmatrix} J_c' & 1 & J_c \\ 3 & J_c & 3 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda' J_c'\rangle\langle\lambda' J_c'\|M^{[3]}\|gJ_c\rangle}{[\Delta E(\lambda' J_c')]^2}. \tag{59}$$

Notice, again, that there is no adiabatic term in the third-rank tensor portion of $E^{[2]}$. This is similar to the vector term and suggests that all odd-order adiabatic contributions will be zero. To date, no experimental evidence of such third-rank tensor structure has been seen. As with the vector structure, it is possible that magnetic structure, in this case magnetic octupole structure, could compete with third-rank electric fine structure. This would be expected to be proportional to the permanent octupole moment of the core ion (requiring $J_c > 1$) and to the inverse fifth power of the Rydberg radial coordinate.

For $b = 4$, the leading term from Sec. II A is proportional to the core's hexadecapole moment. For consistency, the terms in the effective potential of this order are also written as proportional to

$$\frac{\langle X^{[4]}(J_c)\cdot C^{[4]}(\hat{r})\rangle}{\begin{pmatrix} J_c & 4 & J_c \\ -J_c & 0 & J_c \end{pmatrix}}. \tag{60}$$

The energy thus becomes

$$E_4^{[2]}(nL_K) = -\frac{1}{2}((\alpha_{Q,4} + \alpha_{DO,4})\langle r^{-6}\rangle_{nL} + (\alpha_{O,4} - 6\beta_{Q,4} + \alpha_{QH,4} - 6\beta_{DO,4})\langle r^{-8}\rangle_{nL})\frac{\langle X^{[4]}(J_c)\cdot C^{[4]}(\hat{r})\rangle}{\begin{pmatrix} J_c & 4 & J_c \\ -J_c & 0 & J_c \end{pmatrix}}, \tag{61}$$

where

$$\alpha_{Q,4} = \frac{18}{5}\sqrt{\frac{10}{7}}\begin{pmatrix} J_c & 4 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 2 & J_c \\ 4 & J_c & 2 \end{Bmatrix}\frac{\langle gJ_c\|M^{[2]}\|\lambda' J_c'\rangle^2}{\Delta E(\lambda' J_c')}, \tag{62}$$

$$\alpha_{O,4} = -18\sqrt{\frac{2}{77}}\begin{pmatrix} J_c & 4 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 3 & J_c \\ 4 & J_c & 3 \end{Bmatrix}\frac{\langle gJ_c\|M^{[3]}\|\lambda' J_c'\rangle^2}{\Delta E(\lambda' J_c')}, \tag{63}$$

$$\alpha_{DO,4} = 24\sqrt{\frac{1}{7}}\begin{pmatrix} J_c & 4 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{2J_c'}\begin{Bmatrix} J_c' & 1 & J_c \\ 4 & J_c & 3 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda' J_c'\rangle\langle\lambda' J_c'\|M^{[3]}\|gJ_c\rangle}{\Delta E(\lambda' J_c')}, \tag{64}$$

$$\alpha_{QH,4} = -24\sqrt{\frac{5}{77}}\begin{pmatrix} J_c & 4 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{2J_c'}\begin{Bmatrix} J_c' & 2 & J_c \\ 4 & J_c & 4 \end{Bmatrix}\frac{\langle gJ_c\|M^{[2]}\|\lambda' J_c'\rangle\langle\lambda' J_c'\|M^{[4]}\|gJ_c\rangle}{\Delta E(\lambda' J_c')}, \tag{65}$$

$$\beta_{Q,4} = \frac{3}{2}\sqrt{\frac{10}{7}}\begin{pmatrix} J_c & 4 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{J_c'+J_c}\begin{Bmatrix} J_c' & 2 & J_c \\ 4 & J_c & 2 \end{Bmatrix}\frac{\langle gJ_c\|M^{[2]}\|\lambda' J_c'\rangle^2}{[\Delta E(\lambda' J_c')]^2}, \tag{66}$$

$$\beta_{DO,4} = 10\sqrt{\frac{1}{7}}\begin{pmatrix} J_c & 4 & J_c \\ -J_c & 0 & J_c \end{pmatrix}\sum_{\lambda',J_c'}(-1)^{2J_c'}\begin{Bmatrix} J_c' & 1 & J_c \\ 4 & J_c & 3 \end{Bmatrix}\frac{\langle gJ_c\|M^{[1]}\|\lambda' J_c'\rangle\langle\lambda' J_c'\|M^{[3]}\|gJ_c\rangle}{[\Delta E(\lambda' J_c')]^2}. \tag{67}$$

The two terms proportional to r^{-6} agree with the results of Clark, Greene, and Miecznik [12]. The other terms are new.

This completes the list of terms which contribute to $E^{[2]}$ proportional to r^{-s} with $s \leqslant 8$, as long as $J_c < 3$. This is sufficient to account for all cases studied experimentally to date. The full effective potential to this point consists of the sum of all the second-order terms listed above plus the two first-order terms from Sec. II A.

C. Rydberg intermediate states

The expression for the second-order perturbation energy derived in Sec. II B excluded the contributions to $E^{[2]}$ from intermediate states where the core was in its ground electronic state. The number of such states depends on the ion in question. For an ion with an S-state ground electronic state, for example, there is only one ground state. However, for ions with higher angular momentum there may be two or more fine-structure levels within the same electronic state. For example, the ion Ar^+ has a $^2P_{3/2}$ ground state and a $^2P_{1/2}$ excited level within the same electronic state. We consider any state of the combined system in which the core is in the ground electronic state to be a "Rydberg state" and denote it by

$$(gJ_c')n'L_K'. \tag{68}$$

The contribution of such states to the second-order perturbation energy, omitted in Sec. II B, is given by

$$E_{\mathrm{RS}}^{[2]}(nL_K) = -\sum_{J_c',n',L'}{}' \frac{\langle (gJ_c)nL_K|V|(gJ_c')n'L_K'\rangle\langle (gJ_c')n'L_K'|V|(gJ_c)nL_K\rangle}{\Delta E(gJ_c') + E(n') - E(n)}, \tag{69}$$

where the prime on the summation symbol indicates that the intermediate states do not include the initial state $(gJ_c)nL_K$. This term describes the shift in energy of a particular Rydberg level $(gJ_c)nL_K$ due to its coupling with other Rydberg states, either bound to the same core fine-structure level (J_c) or to a different fine-structure level (J_c'). Note that only the even operators in V give nonzero results given the constraints due to parity. In low-L Rydberg levels, it is usual for these couplings to be strong, leading to perturbation of one Rydberg series by another. When these perturbations are strong compared to the spacing between adjacent Rydberg states, they make it necessary to describe the Rydberg structure using the formalism of multi-channel quantum defect theory. In high-L Rydberg levels the effects of these couplings are generally very small, partly because all the matrix elements of V decrease rapidly with L. For example, even the diagonal elements of the leading multipole (quadrupole) term in V decrease approximately as L^{-3}. Thus, as L increases, all the effects of interseries coupling decrease rapidly and become small corrections to the Rydberg energies. Of course, an exception would occur if, by chance, two Rydberg states bound to two different core levels happened to be very nearly degenerate so that even a small coupling matrix element would produce a large shift in energy. Another possible near degeneracy arises between Rydberg levels bound to the core ground state (J_c) and having the same n but different L. One might assume that the quadrupole term in V would lead to strong coupling between the $(J_c)nL_K$ and $(J_c)n(L\pm 2)_K$ levels, which are nearly degenerate even after the first-order perturbation energies are applied. However, in this case, the quadrupole coupling is identically zero for hydrogenic wave functions because of the selection rule

$$\left\langle nL\left|\frac{1}{r^3}\right|n,L\pm 2\right\rangle = 0. \tag{70}$$

Higher permanent moments could, in principal, couple such levels, but in practice the energies of these Rydberg levels differ as a result of the first- and second-order energies discussed in Secs. II A and II B above. The weak couplings due to the hexadecapole and higher multipoles in V produce only very minor energy shifts even when $J_c' = J_c$ and $n' = n$. The main effect of the quadrupole couplings is through nondegenerate intermediate states. It is given by

$$\begin{aligned} E_{\mathrm{RS}}^{[2]}(QQ) &= -\sum_{J_c',n',L'}{}' \frac{\left\langle (gJ_c)nL_K\left|M^{[2]}\cdot\frac{C^{[2]}(\hat{r})}{r^3}\right|(gJ_c')n'L_K'\right\rangle\left\langle (gJ_c')n'L_K'\left|M^{[2]}\cdot\frac{C^{[2]}(\hat{r})}{r^3}\right|(gJ_c)nL_K\right\rangle}{\Delta E(gJ_c') + E(n') - E(n)} \\ &= -\sum_{J_c',n',L'}{}' \begin{Bmatrix} K & L & J_c \\ 2 & J_c' & L' \end{Bmatrix}^2 \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 (2L+1)(2L'+1)\langle gJ_c\|M^{[2]}\|gJ_c'\rangle^2 \frac{[nL|r^{-3}|n'L']^2}{\Delta E(gJ_c') + E(n') - E(n)}. \end{aligned} \tag{71}$$

Evaluation of this expression requires the off-diagonal matrix elements of the quadrupole operator between the ground-state fine-structure levels. The diagonal element is easily estimated from the gross features of the high-L Rydberg fine structure, which reveal the ground-state quadrupole moment. Assuming that the ground-state levels are approximately LS coupled leads to an estimate of the off-diagonal element that is typically of sufficient precision. The selection rules for couplings due to the quadrupole term are $\Delta J_c = 0, \pm 1, \pm 2$, and $\Delta L = 0, \pm 2$.

The primary difficulty in evaluating Eq. (71) is carrying out the sum over n', which includes both discrete and continuum levels. Because of the quadratic dependence of the centrifugal potential on L', the $L' = L + 2$ sum is especially dependent on the continuum contributions. The sum may be evaluated by explicit summation over a range of discrete levels and integration over continuum levels. Alternatively, it can be evaluated using the method of Dalgarno and Lewis [19] where

$$\sum_{n'} \frac{[nL|r^{-s}|n'L'][n'L'|r^{-q}|nL]}{\Delta E(gJ_c') + E(n') - E(n)} = \langle nL|r^{-s}|f(r)\rangle, \tag{72}$$

where the function $f(r)$ is the first-order correction to the wave function $|nL\rangle$ and satisfies a differential equation specific to each (J_c', L') series [20].

The results of Secs. II A and II B can be described as an effective potential in the space of Rydberg levels whose expectation value gives the most important contributions to the Rydberg energies. Since the quadrupole term is the leading term in the effective potential and Eq. (69) describes its effect through mixing different Rydberg levels, it begins to represent application of the effective potential in "second order" within the space of Rydberg levels. It is useful to consider whether other terms in the effective potential could also have significant effects of this type.

The simplest example of this is the shift caused by application of the leading scalar term in V_{eff} proportional to $\alpha_{D,0}$. This was considered by Drachman in his treatment of the case of helium Rydberg levels ($J_c = 0$). He showed that the lowest multipole term in the fourth-order perturbation energy containing an intermediate Rydberg level corresponded, after making the adiabatic approximation to the two other energy denominators, to application of the $\alpha_{D,0}$ term in second order, giving the result

$$E^{[4]}(nL_K) = -\sum_{n'} \frac{\left\langle (gJ_c)nL_K \middle| -\frac{1}{2}\frac{\alpha_{D,0}}{r^4} \middle| (gJ_c)n'L_K \right\rangle^2}{E(n') - E(n)} + \cdots. \tag{73}$$

This led to a significant shift of the energy levels in helium [6]. The shift is a universal function of (n,L) and $\alpha_{D,0}$, and it was later evaluated analytically by Drake and Swainson [21].

In considering the more general case of $J_c \geqslant 0$, the leading terms in the effective potential have the form

$$V_{\mathrm{eff}} \approx -\frac{1}{2}\frac{\alpha_{D,0}}{r^4} - \left(\frac{Q}{r^3} + \frac{1}{2}\frac{\alpha_{D,2}}{r^4}\right) \frac{X^{[2]}(J_c) \cdot C^{[2]}(\hat{r})}{\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}}. \tag{74}$$

The terms proportional to the scalar and tensor dipole polarizabilities also have the potential to mix different Rydberg series and produce energy shifts to a particular level. These energy shifts occur formally as parts of the third- and fourth-order perturbation in V. They are likely the largest contributions from third- and fourth-order perturbation since they include contributions of one intermediate state where the core is not electronically excited. Terms proportional to $Q\alpha$ occur in the third-order perturbation energy, while terms proportional to $\alpha\alpha$ occur in the fourth-order perturbation energy. Both types of terms include one Rydberg intermediate level [denoted $(gJ_c')n'L_K'$ in Eq. (75)] and contain the factor

$$\sum_{\lambda'', J_c'', n'', L''} \frac{\left\langle (gJ_c)nL_K \middle| M^{[1]} \cdot \frac{C^{[1]}(\hat{r})}{r^2} \middle| (\lambda'' J_c'')n''L_K'' \right\rangle \left\langle (\lambda'' J_c'')n''L_K'' \middle| M^{[1]} \cdot \frac{C^{[1]}(\hat{r})}{r^2} \middle| (gJ_c')n'L_K' \right\rangle}{\Delta E(\lambda'' J_c'')}, \tag{75}$$

which can be shown to be equal to

$$\left\langle (gJ_c)nL_K \middle| \frac{1}{2}\frac{\alpha_{D,0}}{r^4} + \frac{1}{2}\frac{\alpha_{D,2}(J_c')}{r^4} \frac{X^{[2]}(J_c) \cdot C^{[2]}(\hat{r})}{\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}} \middle| (gJ_c')n'L_K' \right\rangle, \tag{76}$$

where the reduced matrix elements of $X^{[2]}(J_c)$, both diagonal and off-diagonal in J_c, are equal to 1. The coefficient $\alpha_{D,0}$ is the usual scalar polarizability, given in Sec. II B, and the term proportional to it satisfies the selection rules $\Delta J_c = \Delta L = 0$. The coefficient $\alpha_{D,2}$ (J_c') is given by the expression

$$\alpha_{D,2}(J_c') = 2\sqrt{\frac{10}{3}} \begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix} (-1)^{J_c' - J_c} \sum_{\lambda'', J_c''} (-1)^{2J_c''} \begin{Bmatrix} J_c'' & 1 & J_c \\ 2 & J_c' & 1 \end{Bmatrix} \frac{\langle gJ_c \| M^{[1]} \| \lambda'' J_c'' \rangle \langle \lambda_c'' J_c'' \| M^{[1]} \| gJ_c' \rangle}{\Delta E(\lambda'' J_c'')}. \tag{77}$$

Note that this reduces to the result shown in Sec. II B if $J_c' = J_c$, i.e., for terms diagonal in J_c, but it differs for nondiagonal terms. For example, if $J_c = 5/2$, there are contributions to $\alpha_{D,0}$ and $\alpha_{D,2}$ from branches with $J_c' = 3/2$, $5/2$, and $7/2$, but an off-diagonal $\alpha_{D,2}$ coupling to levels with $J_c' = 3/2$ can have no contribution from the $J_c' = 7/2$ branch. This restriction is enforced by the $6J$ symbol in Eq. (77). This term satisfies the same selection rules as the quadrupole term: $\Delta J_c = 0, \pm 1, \pm 2$, and $\Delta L = 0, \pm 2$.

This implies that the leading "second-order" effects of V_{eff} can be written as

$$E_{\mathrm{eff}}^{[2]}(nL_K) = \sum_{J_c', n', L'}{}' \frac{\langle (gJ_c)nL_K | V_{\mathrm{eff}} | (gJ_c')n'L_K' \rangle \langle (gJ_c')n'L_K' | V_{\mathrm{eff}} | (gJ_c)nL_K \rangle}{\Delta E(gJ_c') + E(n') - E(n)}, \tag{78}$$

where

$$V_{\mathrm{eff}} \approx -\frac{1}{2}\frac{\alpha_{D,0}}{r^4} - \left(\frac{Q(J_c')}{r^3} + \frac{1}{2}\frac{\alpha_{D,2}(J_c')}{r^4}\right) \frac{X^{[2]}(J_c) \cdot C^{[2]}(\hat{r})}{\begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}}, \tag{79}$$

in which $\alpha_{D,2}(J_c')$ is given by Eq. (77) and

$$Q(J_c') = (-1)^{J_c' - J_c} \sqrt{\frac{2J_c' + 1}{2J_c + 1}} \frac{\begin{Bmatrix} S_c & L_c & J_c \\ 2 & J_c' & L_c \end{Bmatrix}}{\begin{Bmatrix} S_c & L_c & J_c \\ 2 & J_c & L_c \end{Bmatrix}} \langle gJ_c \| M^{[2]} \| gJ_c \rangle \begin{pmatrix} J_c & 2 & J_c \\ -J_c & 0 & J_c \end{pmatrix}, \tag{80}$$

where L_c and S_c are the assumed L and S values, respectively, for the core ground electronic state. This expression reduces to the usual quadrupole moment for diagonal terms and gives the result indicated by pure LS coupling for the off-diagonal quadrupole coupling.

When $E^{[2]}{}_{\rm eff}$ [Eq. (78)] is evaluated, it reduces to terms analogous to Eq. (71) while containing sums like Eq. (72) with $(s,q) = (3,3)$, (3,4), and (4,4). The higher inverse powers generally correspond to smaller shifts, and examining the dependence of the calculated shift on the total inverse power can provide a clue to the probable precision of a result truncated with these terms. If necessary, higher terms in $V_{\rm eff}$ can also be included.

D. Spin and relativistic terms

There are several small additional terms not included in the nonrelativistic model described above. The first is the standard relativistic correction to the kinetic energy of a hydrogenic Rydberg electron, given by

$$E_{\rm rel} = \frac{\alpha_{\rm FS}^2 Q^2}{2n^4}\left(\frac{3}{4} - \frac{n}{L+\frac{1}{2}}\right), \tag{81}$$

where $\alpha_{\rm FS}$ is the fine-structure constant. This term is due to the "p^4" contributions to the kinetic energy.

The next two terms describe the magnetic interaction between the Rydberg electron and the core ion's magnetic moments. The dominant effect is due to the magnetic dipole moment of the core, given by

$$E_{{\rm core}M1} = \left\langle -\frac{g_J\alpha_{\rm FS}^2}{2r^3}\vec{L}\cdot\vec{J}_c\right\rangle, \tag{82}$$

where g_J is the core's g value. This term is generally much larger than the electric vector terms discussed in Sec. II B. Another possible magnetic interaction with the core ion is through its permanent magnetic octupole moment. An octupole moment could occur in any ion with $J_c > 1$ and thus contribute to the Rydberg fine structure through a term similar to the third-order tensor terms in $V_{\rm eff}$. We will simply parametrize such a term as

$$E_{{\rm core}M3} = \left\langle \frac{C_{M3}}{r^5}(X^{[3]}(J_c)\cdot T^{[3]}(\hat{r}))\right\rangle, \tag{83}$$

where $T^{[3]}(\hat{r})$ is defined in Eq. (55).

An additional magnetic interaction is with the magnetic moment of the Rydberg electron, either through spin-orbit interaction from its own orbital motion or with the magnetic field from the core ion's magnetic moment. These are given by

$$E_{S_R} = \left\langle \frac{\alpha_{\rm FS}^2}{2r^3}[\vec{L}\cdot\vec{S}_R + g_J\vec{J}_C\cdot(1-3\hat{r}\hat{r})\cdot\vec{S}_R]\right\rangle, \tag{84}$$

where $\vec{S}_R$ is the Rydberg spin. This interaction splits the nL_K level into two states with $J = K \pm \frac{1}{2}$.

All of these terms make only small contributions to the energy of a nonpenetrating Rydberg electron since such an electron is very nonrelativistic.

III. DISCUSSION

The main application of the effective potential model is to provide a framework for extracting measurements of core ion properties from experimental measurements of high-L Rydberg fine-structure patterns. A good example of this is a recent study of argon Rydberg levels [16]. In that study, the relative positions of twenty Rydberg levels within the $n = 10$ manifold with $5 \leqslant L \leqslant 9$ were measured with precision of better than 1 MHz. This pattern of level positions, which spanned a range of more than 25 000 MHz, could be expected to represent the expectation value of the effective potential generated by interactions with the Ar$^+$ core ion. More precisely, this would be the case except for the small level shifts represented by the relativistic corrections in Eq. (81) and the second-order effects of $V_{\rm eff}$ from Eq. (78). Calculation of $E^{[2]}{}_{\rm eff}$, of course, requires some level of knowledge of the core parameters. Rough values may be obtained by initially assuming that $E^{[2]}{}_{\rm eff}$ is zero. It is then calculated using these approximate numbers, and the process repeated until consistent values of the core parameters are found. Table V of Ref. [16] shows the effect of these small corrections and the results once they are removed from the observed pattern. The calculated contributions of $E^{[2]}{}_{\rm eff}$ are small, and decrease smoothly with L, indicating that the influence of mixing between different Rydberg series is relatively minor.

Once the corrections were removed, the data pattern could be decomposed into the contributions of scalar, vector, and tensor orders, defining the structure factors shown in Table VI of Ref. [16]: $A_0(L)$, $A_1(L)$, and $A_2(L)$. Note that since Ar$^+$ has a $^2P_{3/2}$ ground state, a third-order contribution to the structure is possible. A satisfactory fit of the data pattern, however, was obtained without including this term. The variation of the structure factors with L was then used, in combination with the form of the effective potential, to extract experimental estimates of the leading core properties. For example, the tensor structure factor $A_2(L)$ is expected to be dominated by a contribution proportional to $\langle r^{-3}\rangle_{nL}$, with smaller contributions proportional to $\langle r^{-4}\rangle_{nL}$ and perhaps $\langle r^{-6}\rangle_{nL}$. Thus scaling the measured $A_2(L)$ factors by $\langle r^{-3}\rangle_{nL}$ and plotting the ratio versus $\langle r^{-4}\rangle_{nL}/\langle r^{-3}\rangle_{nL}$ leads to the plot shown in Fig. 7 of Ref. [16], from which core properties Q and $\alpha_{D,2}$ were both determined. A similar scaled plot of $A_1(L)$, Fig. 8 in Ref. [16], determined the g_J value of Ar$^+$ and the core property $\beta_{D,1}$. The $A_0(L)$ plot is slightly more complicated since only the relative positions of the twenty levels were measured experimentally. Consequently, only differences of A_0 factors are significant. Still, a plot of $A_0(L+1)$-$A_0(L)$ scaled to the difference of expectation values of r^{-4} was used to determine $\alpha_{D,0}$ from the experimental measurements, and is shown in Fig. 9 of Ref. [16]. In all cases, the appearance of the scaled plots was completely consistent with the expectations based on the form of the effective potential. The precision of the core properties derived in this way is remarkable. The quadrupole moment, Q, was determined to 0.004% while the scalar polarizability, $\alpha_{D,0}$, was determined to 0.03%. Measurements of comparable properties of neutral atoms are difficult or impossible to obtain at this precision. Measurements of these ion properties pose a challenging test of even the most advanced theoretical methods. Confidence in the form of the effective potential is an important factor in analyzing such experimental measurements.

One limitation of the derivation presented in Sec. II is its reliance on the convergence of the adiabatic expansion. Recall that this is based on the dominance of the core excitation energy, $\Delta E(\lambda' J_c')$, in the denominator of the second-order perturbation energy as compared to the difference of Rydberg energies, $E(n')$-$E(n)$, that also occurs there. It is possible to predict the failure of this expansion in a particular case by using the properties of Rydberg electrons to estimate the typical value of the second quantity. Using the case where $\kappa_1 = \kappa_2 = 1$ as an example, the "average" Rydberg energy difference can be estimated using Eqs. (19) and (20):

$$[E(n') - E(n)]_{\mathrm{AV}} = \frac{\sum_{n'} [E(n') - E(n)]\langle nL|r^{-2}|n'L'\rangle^2}{\sum_{n'} \langle nL|r^{-2}|n'L'\rangle^2} = \frac{1}{2}[4 - L(L+1) + L'(L'+1)]\frac{\langle r^{-6}\rangle_{nL}}{\langle r^{-4}\rangle_{nL}}. \tag{85}$$

If the ratio of this average Rydberg energy difference and the lowest core excitation is small, then the adiabatic expansion is likely to converge well. Take for example the $n = 10$ and $L = 6$ Rydberg level of a neutral Rydberg system. In this case the average Rydberg energy difference is $+\,2897$ cm^{-1} if $L' = 7$ and $-\,1287$ cm^{-1} if $L' = 5$. If the core ion is He$^+$, where the lowest dipole excitation is 329 179 cm^{-1}, this suggests rapid convergence of successive terms of the adiabatic expansion. If the core ion is Sr$^+$, where the lowest dipole excitation is 14 556 cm^{-1}, convergence is likely to be less rapid. Of course, since the ratio of expectation values of r^{-6} and r^{-4} decreases rapidly with L, higher L Rydberg levels of the same n should show more rapid convergence.

Fortunately, if a case of nonconvergence of the adiabatic expansion is encountered, the cause is often a single low-lying excited core level with a known position, and this suggests a fairly simple solution. The contribution to the second-order perturbation energy from intermediate states containing this single excited core level can be calculated separately and added to the expectation value of the effective potential, which still describes the contributions of all other intermediate states. The calculated contribution from states containing the specific low-lying core level must be calculated individually for each Rydberg level of interest, and its dependence on n, L, and K may be very different from the form predicted by the effective potential. It is also usually known only up to a constant that represents the square of the matrix element coupling the core ground state to the low-lying state of interest. This constant can be treated as an additional parameter in matching observed fine-structure patterns to the form predicted by the effective potential. This procedure was followed by Gallagher, Kachru, and Tran [4] and Snow and Lundeen [22] in their analysis of the barium Rydberg spectrum. In this case the offending low-lying level is the $5d$ level, which dominates the quadrupole polarization energies.

Another issue that has arisen in analysis of Rydberg spectra involves the problem of fitting the fine-structure pattern's dependence on L to a sequence of inverse powers of r, as briefly described above. While the expectation value of each successive inverse power of r decreases smoothly with L, the variation between r^{-4} and r^{-6} or between r^{-6} and r^{-8} is much more dramatic than between r^{-6} and r^{-7}. It may be possible to fit the data pattern to a sum of contributions proportional to r^{-4}, r^{-6}, and r^{-8}, but impossible to distinguish possible contributions proportional to r^{-7} or to the very similar $L(L + 1)r^{-8}$. This problem is exacerbated by the possibility of an additional contribution proportional to r^{-7} coming from the lowest multipole adiabatic third-order perturbation energy which gives rise to a term proportional to a quantity "δ," discussed in Ref. [23]. This is most significant when it is desired to extract a reliable measurement of the coefficient of r^{-6} in the pattern of experimental energies, as in Si^{2+} [23] or Th^{3+} [24].

The effective potential derived here is similar to the potential derived by Clark, Greene, and Miecznik in the case of nondegenerate channels [their Eq. (20)] [12]. Their potential contains terms up to the inverse sixth power of the Rydberg radial coordinate, and all of their adiabatic terms agree with ours. Their nonadiabatic terms, however, differ slightly from our analogous results. The potential of their Eq. (20) represents the simplest form of their description of high-L Rydberg spectroscopy. Still, by numerically finding the eigenvalues in that potential, one would already include some terms which in our formulation would be included in our $E^{[2]}{}_{\mathrm{eff}}$, i.e., the effects of mixing between Rydberg levels of the same L but different n all coupled to the ground state of the ion core. Clark, Greene, and Miecznik continue by describing more complex formalisms in which the coupling to other channels corresponding to different values of L and perhaps J_c, but the same value of K, are also included prior to numerical solution of the eigenvalue problem. Without a doubt, a calculation based on these more complex formalisms should be more successful in describing the structure of Rydberg levels where coupling between different Rydberg series is significant. Whether this is necessary to describe a particular Rydberg system will depend on the details of the Rydberg core interactions.

One interesting feature of the effective potential is the presence of odd-order tensor interactions, both vector and third-order. The vector terms in high-L Rydberg structure have an extensive history. The first clear observation of such effects occurred in a study of high-L Rydberg states of barium by Gallagher, Kachru, and Tran [4]. In this case the core ion was a $^2S_{1/2}$ state, and large splittings were observed between the two possible values of $K = L \pm \frac{1}{2}$. The observed splittings were much larger than could be accounted for by the expected magnetic interactions. Some years later, stimulated by related, but much smaller, anomalies in the structure of high-L Rydberg levels of Si^{2+}, these vector splittings were explained as an indirect effect of the spin-orbit splittings in excited ^2P levels of Ba$^+$ [25]. These indirect spin-orbit splittings, or K-splittings as they were also called, were later exploited to extract precise measurements of dipole and quadrupole transition strengths in Ba$^+$ [26–28]. In the meantime, an apparently different type of vector splitting was predicted by Zygelman [15] using a Berry phase argument. This splitting was thought to be limited to cases where the core ion had nonzero orbital angular momentum. It was later rederived and calculated more definitively by Clark, Greene, and Miecznik [12], who coined the name "vector hyperpolarizability" to describe it. This is precisely the term represented in Eq. (39) in Sec. II B that is proportional to the coefficient $\beta_{D,1}$. Experimental measurements first in neon [17] and later in argon [16] displayed contributions of this type, vector terms proportional to r^{-6}, and confirmed the coefficient calculated by Clark, Greene, and Miecznik [12]. The argon measurements also suggested that higher-order terms proportional to r^{-8} might be present, as is now predicted by Eq. (39) in Sec. II B. These two types of vector interactions, indirect spin-orbit and vector hyperpolarizability, showed many superficial similarities. They were both proportional to r^{-6} in lowest order, and both were traced to nonadiabatic response of the core to the Rydberg electron. However, the vector hyperpolarizability was thought to require a nonzero core angular momentum, and would therefore be absent in the barium Rydberg states. In fact, they are both described by Eq. (39) of Sec. II B. When the coefficients $\beta_{D,1}$ and $\beta_{Q,1}$ are evaluated for the case of a $^2S_{1/2}$ core ion, they reproduce the results given in Eqs. (15) and (22) of Ref. [25]. We note that, for this case, both coefficients would be zero in the absence of spin-orbit splittings in the excited states of the core, as emphasized by the appearance of Eqs. (15) and (22) of Ref. [25]. Yet, the two effects, thought to be quite different, are truly aspects of the same physical effect.

Another issue is the completely nonrelativistic derivation of the effective potential. One may question whether it is reasonable to expect that the calculation based on a completely nonrelativistic Hamiltonian will describe Rydberg levels in a system where the core ion's nuclear charge is large, thus making the core electrons relativistic even if the Rydberg electron is nonrelativistic. In the absence of a fully relativistic calculation describing the complete Rydberg system, there is no way to answer this question definitively. However, it seems plausible that the physical properties of the core, polarizabilities and permanent moments, would exist even for a highly relativistic core ion, and would interact in a similar way with the nonrelativistic Rydberg electron. These properties, of course, could never be accurately calculated within the nonrelativistic model used in this paper, but would instead require much more sophisticated relativistic formulations of atomic structure theory. There is some circumstantial evidence to suggest that the form of the potential is correct even if the core ion is highly relativistic and that it is still correct to use the form of the potential to interpret the spectroscopy of nonpenetrating Rydberg electrons to extract core properties, even of highly relativistic positive ions. The strongest evidence along these lines is the agreement between the dipole polarizabilities of Pb^{2+} and Pb^{4+} extracted from spectroscopy of high-L Rydberg levels of Pb II and Pb IV [29] and the calculated values obtained using relativistic many-body perturbation theory [30]. The experimental values were 13.62(8) and 3.61(4) a.u. [29] and the calculated values were 13.30 and 3.63 [30]. There is, as yet, no comparable comparison for Rydberg states bound to highly relativistic core ions with nonzero orbital angular momentum.

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