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Quantum defects and the $1/n$ dependence of Rydberg energies: Second-order polarization effects

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The principal result of this paper is a general expression for the second-order dipole polarization energy of a Rydberg electron resulting from the term $-\alpha_1/r^4$ in the asymptotic potential, where α_1 is the core polarizability. It is shown that the second-order term contributes *even* as well as *odd* powers of $1/n$ in a $1/n$ expansion of the energies for Rydberg states. The results are used to extend the interpretation of the terms in a quantum-defect expansion. It is shown that the Ritz expansion for the quantum defect, which contains only *even* inverse powers of the effective quantum number n^*, provides a powerful method for deducing the *even*-order terms in the second-order energy. Least-squares fits to high-precision variational calculations for the Rydberg states of helium, using $1/n$ and quantum-defect expansions, are presented. The results reveal well-defined "Ritz defects," which represent the degree to which the data cannot be represented by a Ritz expansion for the quantum defect. The implications for extrapolations of quantum defects are discussed. Finally, it is shown that the second-order polarization energy plays a significant role in understanding the quantum defects for the alkali metals.

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I. INTRODUCTION

The quantum-defect method [1] is now well established as the method of choice for the analysis of experimental data on the term energies of Rydberg sequences of states. A vast literature has grown up around its many varied applications [2]. However, advances over the past ten years in the precision of both experimental measurements [3–12] and theoretical calculations [13–17] raise new questions concerning the ultimate limits of the quantum-defect method, and in particular the Ritz expansion for the quantum defect, as a suitable functional form for the representation of data.

This paper has three main purposes. The first is to extend the physical identification that can be made for the terms in the Ritz expansion of the quantum defect, especially those arising from second-order polarization effects. Exact analytic results are obtained in Sec. III for the second-order dipole polarization term and compared with the predictions of quantum-defect theory. It is shown in Sec. IV that the second-order term is important in the analysis of data if the core polarizability is large. The second purpose is to apply these results in Sec. IV to recent high-precision calculations [13–15] for the Rydberg P, D, and F states of helium, and to identify what extensions of the usual Ritz expansion might be necessary. The third is to identify the conditions under which the Ritz expansion is no longer capable of representing data in the broader context of quasihydrogenic spectra. Not considered are the more general problems of multiple Rydberg series and their perturbations [2].

II. QUANTUM-DEFECT THEORY AND $1/n$ EXPANSIONS

As first pointed out by Ritz [18], the term energies of a single Rydberg series of states for a quasihydrogenic atom are well represented by the formula

$$T_n = -2R_M/(2n^{*2}) , \tag{1}$$

where R_M is the reduced mass Rydberg constant, $2R_M$ is the reduced mass atomic unit of energy, and n^* is an effective quantum number given by

$$\begin{aligned} n^* &= n - \delta(n^*) \\ &= n - \delta_0 - \frac{\delta_2}{(n-\delta)^2} - \frac{\delta_4}{(n-\delta)^4} - \cdots . \end{aligned} \tag{2}$$

δ is called the "quantum defect." A theoretical justification of this result was given by Sommerfeld [19] based on the old quantum theory, and by Hartree [20] using wave mechanics. The key point proved by Hartree is that if the motion of an electron is describable by a Hamiltonian of the form

$$H = H_c + \lambda V , \tag{3}$$

where H_c is the Hamiltonian for a purely Coulombic potential and λV is a short-range spherically symmetric correction potential, then the eigenvalues of H are given *exactly* by Eq. (1) with only the *even* powers of $1/(n-\delta)$ appearing in Eq. (2). The proof is nonperturbative, and so applies for arbitrary values of the strength parameter λ. As will be shown in Sec. III, this fact can be used to advantage in calculating the general n dependence of the terms in a perturbation expansion containing powers of λ. However, notice that δ appears in the denominators of Eq. (2), rather than δ_0. Replacing δ by δ_0, as is often done in fitting experimental data, may lead to an apparently adequate fit, but it spoils the theoretical significance of the coefficients. It will also ultimately limit the accuracy of the quantum-defect method. This point will be further discussed below and in Secs. III and IV.

The physical significance of the coefficients in the Ritz formula (2) is made evident by expanding Eq. (1) as a power series in $1/n$. Keeping terms up to quadratic in the coefficients, the result is

$$T_n=-2R_M\left[\frac{1}{2n^2}+\frac{\delta_0}{n^3}+\frac{\delta_2}{n^5}+\frac{\delta_4}{n^7}+\frac{\delta_6}{n^9}+\cdots\right.$$
$$+\frac{3\delta_0^2}{2n^4}+\frac{5\delta_0\delta_2}{n^6}+\frac{7}{2n^8}(\delta_2^2+2\delta_0\delta_4)$$
$$\left.+\frac{9}{n^{10}}(\delta_0\delta_6+\delta_2\delta_4)+\cdots\right] . \quad (4)$$

The influence of the δ expansion in the denominators of Eq. (2) first appears in the terms of order $1/n^8$. Replacing δ by δ_0 reduces the coefficient of δ_2^2 from $\frac{7}{2}$ to $\frac{3}{2}$ and the coefficient of $\delta_2\delta_4$ from 9 to 3. It will be shown in Sec. III that the value $\frac{7}{2}$ is in fact correct.

The physical significance of the terms in Eq. (4) now follows from a comparison with the asymptotic potential experienced by the Rydberg electron. In order for a single local potential as in Eq. (3) to be adequate, it is necessary that nonlocal exchange effects be negligible. If in addition the angular momentum L is large enough so that there is little core penetration by the Rydberg electron, then the asymptotic potential has the well-known form [21]

$$V(r)=-\frac{1}{2}\left[\frac{c_4}{r^4}+\frac{c_6}{r^6}+\frac{c_7}{r^7}+\frac{c_8}{r^8}-\cdots\right] , \quad (5)$$

where

$$c_4=\alpha_1 , \quad (6)$$

$$c_6=\alpha_2-6\beta_1 , \quad (7)$$

$$c_7=-\delta'-16\gamma/6 , \quad (8)$$

$$c_8=\alpha_3-15\beta_2+\epsilon-\alpha_1\beta_1+72\gamma[1+L(L+1)/10] . \quad (9)$$

r is the radial coordinate of the Rydberg electron, α_L is the 2^L-pole polarizability, β_L is the corresponding nonadiabatic correction, and the other terms in c_7 and c_8 are higher-order corrections defined by Drachman [21]. The quantities $c_4, c_6, \ldots$ play the role of the strength parameter λ in Eq. (3). The first-order correction to the energy is then

$$E^{(1)}=\langle V\rangle , \quad (10)$$

where the expectation value is with respect to the Rydberg electron. With the notation

$$f_p(L)=(L+p)!/(L-p)! , \quad (11)$$

$$G_p(L)=\frac{2^pZ^p(2L-p+2)!}{(2L+p-1)!} , \quad (12)$$

the general expressions for the expectation values of the powers of $1/r$ in Eq. (5) are [22]

$$\langle r^{-4}\rangle=\frac{G_4(L)}{n^5}[3n^2-f_1(L)] , \quad (13)$$

$$\langle r^{-6}\rangle=\frac{3G_6(L)}{n^7}\{\tfrac{35}{3}n^4-10n^2[f_1(L)-\tfrac{5}{6}]+f_2(L)\} , \quad (14)$$

$$\langle r^{-7}\rangle=\frac{30G_7(L)}{n^8}\{\tfrac{21}{5}n^5-\tfrac{14}{3}n^3[f_1(L)-\tfrac{3}{5}]$$
$$+n[f_2(L)-\tfrac{4}{3}f_1(L)+\tfrac{4}{5}]\} , \quad (15)$$

$$\langle r^{-8}\rangle=\frac{10G_8(L)}{n^9}\{\tfrac{231}{5}n^6-63n^4[f_1(L)-\tfrac{7}{3}]$$
$$+21n^2[f_2(L)-3f_1(L)+\tfrac{14}{5}]-f_3(L)\} . \quad (16)$$

Comparing with Eq. (4) for the odd powers of $1/n$ leads immediately to the first-order identifications

$$\delta_0^{(1)}=\tfrac{3}{2}c_4G_4(L)+\tfrac{35}{2}c_6G_6(L)$$
$$+63c_7G_7(L)+231c_8G_8(L)+\cdots , \quad (17)$$

$$\delta_2^{(1)}=-\tfrac{1}{2}c_4G_4(L)f_1(L)-15c_6G_6(L)[f_1(L)-\tfrac{5}{6}]$$
$$-70c_7G_7(L)[f_1(L)-\tfrac{3}{5}]$$
$$-315c_8G_8(L)[f_1(L)-\tfrac{7}{3}]-\cdots , \quad (18)$$

$$\delta_4^{(1)}=\tfrac{3}{2}c_6G_6(L)f_2(L)+15c_7G_7(L)[f_2(L)-\tfrac{4}{3}f_1(L)+\tfrac{4}{5}]$$
$$+105c_8G_8(L)[f_2(L)-3f_1(L)+\tfrac{14}{5}]+\cdots , \quad (19)$$

$$\delta_6^{(1)}=-5c_8G_8(L)f_3(L)-\cdots , \quad (20)$$

correct to first order in the c_i's. The above are of course asymptotic expansions which must be terminated after a finite number of terms, depending on the value of L.

Except for the nonadiabatic and higher-order corrections contained in c_6, c_7, and c_8, the above identifications coincide exactly with the standard ones discussed for example by Edlén [1] and Curtis [23]. What has not been adequately discussed before is the origin and significance of the *even* powers of $1/n$ in Eq. (4). The coefficients are all quadratic in the δ's. They are uniquely determined once the coefficients of the odd powers have been fixed because Eq. (4) contains twice as many terms as the original Ritz expansion for a given highest power of $1/n$.

In fitting data, it has sometimes been argued that T_n should be written in the form

$$T_n=-2R_M(1/2n^2+a_3/n^3+a_5/n^5+\cdots) , \quad (21)$$

where the *even* terms beyond $1/n^2$ have been dropped. One argument is based on the fact that no inverse power of r (whether *even* or *odd*) in the asymptotic potential can produce *even* powers of $1/n$, and additional exchange and short-range effects not included in Eq. (5) decrease exponentially with n. For example, Chang and Poe [24] fitted their results of many-body perturbation theory (MBPT) calculations for He to a function of this form in order to extrapolate to high n. It has even been argued that the results of nonrelativistic MBPT can be represented exactly in the form of Eq. (21) [25]. However, if Hartree's proof is to be taken seriously, then the *even* terms in Eq. (4) have a significance which cannot be ignored. As shown in Sec. III, they coincide exactly with the second-order perturbation corrections generated by the terms in the asymptotic potential. In fact, Eq. (4) provides a trivial way of calculating them. For example, if Eq. (21) is extended to include the *even* terms $a_4/n^4+a_6/n^6+\cdots$, then Eq. (4) predicts that

$$a_4=3a_3^2/2\ , \tag{22}$$

$$a_6=5a_3a_5\ , \tag{23}$$

and so on for the values implied by the assumed Ritz expansion. If a fit to experimental or theoretical energy levels yields some other value for a_4, say $\tilde{a}_4$, then the difference

$$\Delta a_4=a_4-\tilde{a}_4 \tag{24}$$

is the leading term in what might be called the *Ritz defect.* It represents the degree to which the data cannot be represented in the form of the Ritz expansion for the quantum defect. This result does not depend on the coefficients being small since Hartree's proof is nonperturbative.

The *even* inverse powers also enter when relativistic corrections are included. This is easily seen from the well-known formula for the leading one-electron relativistic energy shift [26]

$$\Delta T_{\rm rel}=-\frac{\alpha^2Z_{\rm eff}^4}{2n^3}\left[\frac{1}{j+\frac{1}{2}}-\frac{3}{4n}\right]\ . \tag{25}$$

A relativistic generalization of the quantum-defect method has been developed by Johnson and Cheng [27]. The presence of the $1/n^4$ term was also noted in passing by Curtis [23] in his semiclassical analysis of the quantum-defect method. If experimental energies or theoretical calculations are analyzed in terms of a $1/n$ expansion, it is important to realize that the *even* inverse powers contain nonrelativistic as well as relativistic contributions.

III. SECOND-ORDER DIPOLE POLARIZATION ENERGY

If the asymptotic expansion (5) is carried to terms of order $\langle r^{-7}\rangle$ and $\langle r^{-8}\rangle$, then one should also include the second-order dipole polarization correction (in atomic units)

$$E^{(2)}=-(\alpha_1/2)\langle\psi_1|r^{-4}|\psi_0\rangle\ , \tag{26}$$

where ψ_0 is the unperturbed wave function for the nL Rydberg electron and ψ_1 satisfies the first-order perturbation equation

$$(H_c+Z_{\rm eff}^2/2n^2)\psi_1-\frac{\alpha_1}{2r^4}\psi_0=-(\alpha_1/2)\langle\psi_0|r^{-4}|\psi_0\rangle\psi_0\ . \tag{27}$$

Numerical values for $E^{(2)}$ have been calculated by Drachman [21] and shown to be important for the Rydberg states of helium. He succeeded in obtaining analytic expressions for $E^{(2)}$ for sequences of states with constant $n-L$, but the general n dependence of $E^{(2)}$ for fixed L has not previously been obtained.

Introducing the scaled quantities

$$x=Z_{\rm eff}r/a_0,\quad \mathcal{E}=E(a_0/e^2)/Z_{\rm eff}^2\ ,$$

where $Z_{\rm eff}$ is the effective nuclear charge experienced by the Rydberg electron, and defining $\tilde{\alpha}_1=Z_{\rm eff}^2\alpha_1/a_0^3$, the radial part of Eq. (27) becomes

$$\left[-\frac{1}{2}\frac{d^2}{dx^2}-\frac{d}{dx}+\frac{L(L+1)}{2x^2}-\frac{1}{x}+\frac{1}{2n^2}\right]u_1(x)-\frac{\tilde{\alpha}_1}{2x^4}u_0(x)=\mathcal{E}^{(1)}u_0(x)\ , \tag{28}$$

where $u_0(x)$ is the radial part of ψ_0 and

$$\mathcal{E}^{(1)}=-(\tilde{\alpha}_1/2)\langle\psi_0|x^{-4}|\psi_0\rangle\ . \tag{29}$$

The assumed normalization condition $\langle\psi_1|\psi_0\rangle=0$ can always be satisfied by adding an appropriate component of u_0 to u_1. The solution to (28) for a particular nL state ($L\geq 2$) is easily found by writing $u_1(x)$ in the form

$$u_1(x)=\frac{\tilde{\alpha}_1}{2}\sum_{j=L-1}^{n+1}g_jx^{j-1}e^{-x/n}+\frac{\tilde{\alpha}_1}{2}\sum_{j=L+1}^{n}h_jx^{j-1}\ln x e^{-x/n}\ . \tag{30}$$

The hydrogenic $u_0(x)$ is given by

$$u_0(x)=\sum_{j=L+1}^{n}A_jx^{j-1}e^{-x/n}\ , \tag{31}$$

with

$$A_{L+1}=\frac{2^{L+1}}{n^{L+2}}\left[\frac{(n+L)!}{(n-L+1)!}\right]^{1/2}\frac{1}{(2L+1)!} \tag{32}$$

and

$$A_{j+1}=\left[\frac{2(j-n)}{n[j(j+1)-L(L+1)]}\right]A_j\ ,\quad j=L+1,\ldots,n-1\ . \tag{33}$$

Substituting into Eq. (28) yields the recursion relations

$$h_{j+1}=\left[\frac{2(j-n)}{n[j(j+1)-L(L+1)]}\right]h_j \tag{34}$$

and

$$g_{j+1}=\frac{2}{[j(j+1)-L(L+1)]}\times\left[\frac{(j-n)}{n}g_j-A_{j+3}+\langle x^{-4}\rangle A_{j-1}-\frac{(2j+1)}{2}h_{j+1}+\frac{1}{n}h_j\right] \tag{35}$$

for $j=L+1,\ldots,n+1$, with the starting values

$$g_{L-1}=A_{L+1}/(2L-1),\quad h_{L-1}=0\ ;$$

$$g_L=\frac{1}{L}\left[A_{L+2}-\frac{(L-n-1)}{n}g_{L-1}\right],h_L=0\ ;$$

$$g_{L+1}=0,\quad h_{L+1}=\frac{2}{(2L+1)}\left[\frac{(L-n)}{n}g_L-A_{L+3}\right]$$

for the unnormalized solution.

The recursion relations (34) and (35) always terminate after a finite number of terms, and so a closed form solution can be found for any particular values of n and L ($n\geq L+1$). However, our aim here is to find the general functional dependence of $E^{(2)}$ on n and L. A direct derivation of the general solution for arbitrary n and L from the recursion relations appears to be a difficult task, even with the use of symbolic manipulation programs such as MACSYMA [21].

To circumvent this difficulty, we have followed the expedient of generating a sufficiently large array of values for $\mathcal{E}^{(2)}$ in quadruple precision arithmetic (32 decimal digits) and deducing the general solution. To this end, values of $\mathcal{E}^{(2)}(n,L)$ were calculated for all $2\leq L\leq 8$ and $L+1\leq n\leq 20$. To proceed from here a great deal can be learned about the form of the general solution from the particular cases

$$\mathcal{E}^{(2)}(n,n-1)=-\frac{2\tilde{\alpha}_1^2(128n^4-560n^3+848n^2-518n+105)}{n^8(2n-5)[(2n-1)(n-1)(2n-3)]^3}\ , \tag{36}$$

$$\mathcal{E}^{(2)}(n,n-2)=-\frac{2\tilde{\alpha}_1^2(128n^7-400n^6-2320n^5+12\,666n^4-19\,133n^3+4846n^2+10\,228n-5880)}{n^8(2n-7)[(n-2)(n-1)(2n-3)(2n-5)]^3}\ , \tag{37}$$

derived by Drachman [21]. These results do not allow one to disentangle the dependence on n and L, but one can extract the coefficients of $1/n^j$ in the expansion

$$\mathcal{E}^{(2)}(n,L)=\sum_j c_j(L)/n^j \tag{38}$$

for fixed L by differencing our numerical values. The result is that only the powers $3\leq j\leq 8$ contribute. As a consequence, none of the factors in the denominators of (36) and (37) can be of the form $(n\pm L+\cdots)$ because this would lead to infinite expansions in $1/n$. They must all be of the form $(2L\pm p)$, where p is an integer. The denominators of (36) and (37) can therefore be written in the forms

$$D(n,n-1)=n^5(2L-3)\times[(2L-1)2L(2L+1)(2L+2)]^3/8 \tag{39}$$

and

$$D(n,n-2)=n^8(2L-3)\times[(2L-1)2L(2L+1)(2L+2)]^3/64\ . \tag{40}$$

With this information in hand, it is relatively easy to identify the numerical coefficients $c_j(L)$ as rational fractions. Observing how the prime factors in the denominators of the $c_j(L)$ change with L for fixed j allows a unique identification with factors of $(2L+p)$. The numerators are more complicated, but they can also be expressed as finite polynomials in L with integer coefficients. The final result is

$$\mathcal{E}^{(2)}(n,L)=-2\tilde{\alpha}_1^2\left[\frac{(2L-3)!!}{(2L+3)!!}\right]^2\left\{\frac{(2L-5)!!}{(2L+5)!!}\frac{1}{n^7}\left[\left[\frac{9n^4}{[L(L+1)]^3}-\frac{6n^2}{[L(L+1)]^2}\right]\times\{45+7[89f_1(L)+520f_2(L)+80f_3(L)]\}+\{3+40[f_1(L)+6f_2(L)]\}\right]+\frac{1}{n^8}\left[\frac{27n^4}{[L(L+1)]^2}-\frac{30n^2}{L(L+1)}+7\right]\right\} \tag{41}$$

where

$$f_1(L)=L(L+1)\;,$$
$$f_2(L)=(L-1)L(L+1)(L+2)\;,$$
$$f_3(L)=(L-2)(L-1)L(L+1)(L+2)(L+3)\;,$$

in accordance with definition (11). Finally $E^{(2)}$ is related to $\mathcal{E}^{(2)}$ by

$$E^{(2)}=Z_{\rm eff}^{6}\mathcal{E}^{(2)}\;. \tag{42}$$

For the Rydberg states of helium, $Z_{\rm eff}=1$ and $\tilde{\alpha}_1=\alpha_1=\frac{9}{32}a_0^3$. The numerical values obtained from the above general formula agree well with those tabulated by Drachman [21]. Explicit formulas for the first few L values are

$$\mathcal{E}^{(2)}(n,2)=\frac{\tilde{\alpha}_1^2}{4[(3)(5)(7)]^3}\left[-\frac{10\,127}{3}\left[\frac{1}{n^3}-\frac{4}{n^5}\right]-\frac{5336}{n^7}\right]+\frac{\tilde{\alpha}_1^2}{2[(3)(5)(7)]^2}\left[-\frac{3}{n^4}+\frac{20}{n^6}-\frac{28}{n^8}\right]\;, \tag{43}$$

$$\mathcal{E}^{(2)}(n,3)=\frac{\tilde{\alpha}_1^2}{44[(5)(7)(9)]^3}\left[-94\,169\left[\frac{1}{8n^3}-\frac{1}{n^5}\right]-\frac{78\,088}{n^7}\right]+\frac{\tilde{\alpha}_1^2}{4[(5)(7)(9)]^2}\left[-\frac{3}{2n^4}+\frac{20}{n^6}-\frac{56}{n^8}\right]\;, \tag{44}$$

$$\mathcal{E}^{(2)}(n,4)=\frac{\tilde{\alpha}_1^2}{260[(7)(9)(11)]^3}\left[-\frac{2\,487\,183}{5}\left[\frac{3}{40n^3}-\frac{1}{n^5}\right]-\frac{697\,624}{n^7}\right]+\frac{\tilde{\alpha}_1^2}{4[(7)(9)(11)]^2}\left[I-\frac{27}{50n^4}+\frac{12}{n^6}-\frac{56}{n^8}\right]\;, \tag{45}$$

$$\mathcal{E}^{(2)}(n,5)=\frac{\tilde{\alpha}_1^2}{140[(9)(11)(13)]^3}\left[-\frac{319\,243}{5}\left[\frac{1}{5n^3}-\frac{4}{n^5}\right]-\frac{540\,808}{n^7}\right]+\frac{\tilde{\alpha}_1^2}{2[(9)(11)(13)]^2}\left[-\frac{3}{25n^4}+\frac{4}{n^6}-\frac{28}{n^8}\right]\;, \tag{46}$$

$$\mathcal{E}^{(2)}(n,6)=\frac{\tilde{\alpha}_1^2}{68[(11)(13)(15)]^3}\left[-\frac{4\,445\,579}{147}\left[\frac{1}{7n^3}-\frac{4}{n^5}\right]-\frac{359\,896}{n^7}\right]+\frac{\tilde{\alpha}_1^2}{2[(11)(13)(15)]^2}\left[-\frac{3}{49n^4}+\frac{20}{7n^6}-\frac{28}{n^8}\right], \tag{47}$$

$$\mathcal{E}^{(2)}(n,7)=\frac{\tilde{\alpha}_1^2}{836[(13)(15)(17)]^3}\left[-\frac{287\,142\,879}{196}\left[\frac{3}{112n^3}-\frac{1}{n^5}\right]-\frac{5\,824\,024}{n^7}\right]+\frac{\tilde{\alpha}_1^2}{4[(13)(15)(17)]^2}\left[-\frac{27}{392n^4}+\frac{30}{7n^6}-\frac{56}{n^8}\right]\;, \tag{48}$$

$$\mathcal{E}^{(2)}(n,8)=\frac{\tilde{\alpha}_1^2}{364[(15)(17)(19)]^3}\left[-\frac{22\,740\,989}{36}\left[\frac{1}{48n^3}-\frac{1}{n^5}\right]-\frac{3\,233\,288}{n^7}\right]+\frac{\tilde{\alpha}_1^2}{4[(15)(17)(19)]^2}\left[-\frac{1}{24n^4}+\frac{10}{3n^6}-\frac{56}{n^8}\right]\;. \tag{49}$$

For the D states of He, the coefficient of the n^{-4} term corresponds to -70.81 MHz and for the F states it corresponds to -1.967 MHz.

In view of the discussion in Sec. II, the *even* powers of n in Eq. (41) are of particular significance. Equation (4) predicts that the leading *even* terms are (in atomic units)

$$T_n(\text{even})=-\left[\frac{3\delta_0^2}{2n^4}+\frac{5\delta_0\delta_2}{n^6}+\frac{7}{2n^8}(\delta_2^2+2\delta_0\delta_4)+\cdots\right]\;. \tag{50}$$

An examination of Eqs. (17)–(20) shows that only δ_0 and δ_2 depend in first order on $c_4=\alpha_1$. Retaining only the α_1 dependence, Eqs. (17) and (18) reduce to

$$\delta_0^{(1)}=\frac{6\alpha_1}{L(L+1)(2L-1)(2L+1)(2L+3)}\;, \tag{51}$$

$$\delta_2^{(1)}=\frac{-2\alpha_1}{(2L-1)(2L+1)(2L+3)}\;. \tag{52}$$

Substituting (51) and (52) into (50) yields

$$T_n(\text{even}) = \frac{-2\alpha_1^2}{n^8(2L-1)(2L+1)(2L+3)} \times \left[\frac{27n^4}{[L(L+1)]^2} - \frac{30n^2}{L(L+1)} + 7 \right], \tag{53}$$

in exact agreement with the corresponding terms in Eq. (41) obtained from the second-order perturbation calculation. This provides a remarkable confirmation that Hartree's proof is an exact analytic result which can be used to advantage in deriving at least the even-n terms in second order perturbation energies. It also verifies the correctness of the coefficient of the n^{-8} term in Eq. (4). The numerical value $\frac{7}{2}$ comes in part from the δ expansion in the denominators of Eq. (2).

IV. COMPARISON WITH THEORETICAL AND EXPERIMENTAL TERM ENERGIES

A. Comparison with nonrelativistic energies for helium

High-precision variational calculations [13–15] and experimental data [12] are now available for the Rydberg states of helium. The purpose of this section is to construct $1/n$ and quantum-defect fits to the data in order to assess the validity of the Ritz expansion, and identify the contributions from $E^{(2)}$.

As a preliminary, Table I shows the orders of magnitude to be expected for the coefficients a_i in the $1/n$ expansion

$$T_n = -2R_M(1/2n^2 + a_3/n^3 + a_4/n^4 + a_5/n^5 + \cdots) \tag{54}$$

for the term energy. The contributions are obtained from Eq. (4), using expressions (17)–(20) for the first-order quantum defects and Eq. (41) for $E^{(2)}$. The totals are obtained from Drachman's [21] prescription for summing these asymptotic series; i.e., the total includes the contribution to a_i from $\frac{1}{2}(c_7\langle r^{-7}\rangle + c_8\langle r^{-8}\rangle)$ with $\pm\frac{1}{2}(c_7\langle r^{-7}\rangle + c_8\langle r^{-8}\rangle)$ being the uncertainty. For $L=2$ and 3, the total includes $\frac{1}{2}c_6\langle r^{-6}\rangle$ with $\pm\frac{1}{2}c_6\langle r^{-6}\rangle$ being the uncertainty. Previous comparisons of the total energies with high-precision variational calculations [15] show that these uncertainty estimates are in good accord with the actual errors resulting from truncating the asymptotic expansion. The numerical values of the core polarizabilities, etc., required to calculate the c_i coefficients in the asymptotic potential are

$$\alpha_1 = \tfrac{9}{32}, \quad \alpha_2 = \tfrac{15}{64}, \quad \alpha_3 = \tfrac{525}{1024},$$

$$\beta_1 = \tfrac{43}{512}, \quad \beta_2 = \tfrac{107}{2048}, \quad \gamma = \tfrac{319}{12\,288},$$

$$\delta' = \tfrac{213}{512}, \quad \varepsilon = \tfrac{4329}{32\,768}.$$

The above values were checked independently and found to agree with those listed by Drachman [21].

Table I shows several interesting features. First, the dramatic increase in the rate of convergence and accura-

TABLE I. Contributions from the asymptotic potential (5) to the coefficients a_i in the $1/n$ expansion $T_n = -2R_M(1/2n^2 + a_3/n^3 + a_4/n^4 + a_5/n^5 + \cdots)$ for the nonrelativistic energies of helium (in 10^{-6} a.u.). L is the angular momentum of the Rydberg state.

Term	Contribution	$L=2$	$L=3$	$L=4$	$L=5$	$L=6$	$L=7$	$L=8$
a_3	$c_4\langle r^{-4}\rangle$	2679.0	446.4	121.75	43.706	18.731 27	9.090 17	4.837 461
	$c_6\langle r^{-6}\rangle$	−832.0	−15.1	−1.16	−0.166	−0.034 22	−0.009 01	−0.002 830
	$c_7\langle r^{-7}\rangle$			−0.28	−0.023	−0.003 17	−0.000 60	−0.000 143
	$c_8\langle r^{-8}\rangle$			0.49	0.029	0.003 35	0.000 57	0.000 126
	$-E^{(2)}$	58.0	0.7	0.03	0.003	0.000 51	0.000 10	0.000 025
	total	2320.0	439.5	120.73	43.547	18.697 65	9.081 26	4.834 648
	uncertainty	±416.0	±7.6	±0.11	±0.003	±0.000 09	±0.000 02	±0.000 009
a_4	$-E^{(2)}$	11.0	0.30	0.022	0.0029	0.000 53	0.000 12	0.000 035
a_5	$c_4\langle r^{-4}\rangle$	−5357.0	−1785.7	−811.69	−437.063	−262.237 8	−169.683 26	−116.099 071
	$c_6\langle r^{-6}\rangle$	3684.0	144.8	19.11	4.155	1.207 5	0.425 82	0.172 643
	$c_7\langle r^{-7}\rangle$			5.69	0.731	0.142 6	0.036 35	0.011 196
	$c_8\langle r^{-8}\rangle$			−11.86	−1.101	−0.180 9	−0.041 58	−0.011 958
	$-E^{(2)}$	−231.0	−5.4	−0.45	−0.068	−0.014 3	−0.003 81	−0.001 207
	total	−3746.0	−1718.7	−796.11	−433.160	−261.063 7	−169.263 86	−115.928 016
	uncertainty	±1842.0	±72.0	±3.1	±0.19	±0.019	±0.002 6	±0.000 38
a_6	$-E^{(2)}$	−72.0	−4.0	−0.49	−0.096	−0.024 56	−0.007 71	−0.002 808
a_7	$c_4\langle r^{-4}\rangle$	0.0	0.0	0.00	0.000	0.000 00	0.000 00	0.000 000
	$c_6\langle r^{-6}\rangle$	−1711.0	−155.6	−35.90	−11.967	−4.927 67	−2.334 16	−1.222 655
	$c_7\langle r^{-7}\rangle$			−22.04	−4.401	−1.225 66	−0.421 66	−0.168 274
	$c_8\langle r^{-8}\rangle$			67.78	9.986	2.367 13	0.738 27	0.276 175
	$-E^{(2)}$	91.0	4.5	0.64	0.143	0.042 42	0.015 13	0.006 178
	total	−765.0	−73.3	−12.39	−9.031	−4.314 51	−2.160 72	−1.162 527
	uncertainty	±856.0	±78.0	±23.0	±2.8	±0.57	±0.16	±0.054
a_8	$-E^{(2)}$	100.0	11.2	2.31	0.669	0.240 69	0.100 77	0.047 176

cy with increasing L is clearly evident. Second, the coefficient a_5 is negative in magnitude and becomes progressively larger with increasing L relative to the other terms. Since $a_3 \simeq \delta_0^{(1)}$ and $a_5 \simeq \delta_2^{(1)}$, the reason for this behavior is clear from the denominators in Eqs. (51) and (52). Third, $E^{(2)}$ makes a relatively small contribution to the odd-order terms, but it is solely responsible for the even-order terms. Since $E^{(2)}$ scales in proportion to α_1^2, it becomes relatively much larger in other hydrogenic atoms such as the alkali metals. For example, $\alpha_1(\mathrm{Cs}^+) \simeq 56.2\alpha_1(\mathrm{He}^+)$ [28]. For $L=2$, this makes the $E^{(2)}$ contribution to a_3 about the same size as the leading $c_4\langle r^{-4}\rangle$ contribution. Even for the D states of helium, omitting the $E^{(2)}$ contribution would reduce the value of α_1 deduced from the measured quantum defect by about 3%. Results for the alkali metals are further discussed below.

Turning now to the numerical fits, Table II lists nonrelativistic eigenvalues for the P, D, and F states of helium, obtained by the double basis set variational calculations described previously [13–15]. A full account of the calculations is in preparation [29]. The exceptional accuracy of the results provides an ideal "experiment," free of relativistic and QED corrections, against which the Ritz expansion can be tested. The following three functional forms, all containing six adjustable parameters, will be compared:

$$T_n = -2R_M(1/2n^2 + a_3/n^3 + a_4/n^4 + a_5/n^5 + a_6/n^6 + a_7/n^7 + a_8/n^8) , \quad (55)$$

$$T_n' = -R_M/(n - \delta_0 - \delta_1/n^* - \delta_2/n^{*2} - \delta_3/n^{*3} - \delta_4/n^{*4} - \delta_5/n^{*5})^2 , \quad (56)$$

$$T_n'' = -R_M/(n - \delta_0 - \delta_2/n^{*2} - \delta_4/n^{*4} - \delta_6/n^{*6} - \delta_8/n^{*8} - \delta_{10}/n^{*10})^2 . \quad (57)$$

T_n corresponds directly to Eq. (54) and the asymptotic numerical values for the coefficients shown in Table I. T_n' contains all inverse powers of n^* in the quantum-defect expansion, while T_n'' contains only the *even* inverse powers (the Ritz expansion).

Beginning with T_n, Table III compares the first two or three fitting coefficients for the P, D, and F states with the asymptotic values from Table I. In every case, the agreement is within the estimated accuracy of the asymptotic coefficients. The "Ritz" value for a_4 corresponds to $a_4 = \frac{3}{2}a_{3,\mathrm{variational}}^2$ [cf. Eq. (22)], and the Ritz defect is as defined by Eq. (24). In each case the Ritz defect is statistically significant, indicating that the variational eigenvalues cannot be represented by a Ritz expansion. However, the agreement is close enough to provide strong confirmation for the calculated $E^{(2)}$ contributions.

The P states are a special case because the asymptotic

TABLE II. Variational nonrelativistic eigenvalues for helium.

State	E (a.u.)	State	E (a.u.)
$2\,^1P$	−2.123 843 086 498 093(10)[a]	$2\,^3P$	−2.133 164 190 779 274(9)
$3\,^1P$	−2.055 146 362 091 944(31)	$3\,^3P$	−2.058 081 084 274 274(34)
$4\,^1P$	−2.031 069 650 450 235(24)	$4\,^3P$	−2.032 324 354 296 619(16)
$5\,^1P$	−2.019 905 989 900 825(22)	$5\,^3P$	−2.020 551 187 256 247(23)
$6\,^1P$	−2.013 833 979 671 734(23)	$6\,^3P$	−2.014 207 958 773 734(12)
$7\,^1P$	−2.010 169 314 529 353(20)	$7\,^3P$	−2.010 404 960 007 936(21)
$8\,^1P$	−2.007 789 127 133 214(18)	$8\,^3P$	−2.007 947 013 771 117(13)
$9\,^1P$	−2.006 156 384 652 846(37)	$9\,^3P$	−2.006 267 267 366 410(42)
$10\,^1P$	−2.004 987 983 802 218(44)	$10\,^3P$	−2.005 068 805 497 766(99)
$3\,^1D$	−2.055 620 732 852 246(6)	$3\,^3D$	−2.055 636 309 453 261(3)
$4\,^1D$	−2.031 279 846 178 687(7)	$4\,^3D$	−2.031 288 847 501 795(3)
$5\,^1D$	−2.020 015 836 159 984(4)	$5\,^3D$	−2.020 021 027 446 911(6)
$6\,^1D$	−2.013 898 227 424 286(4)	$6\,^3D$	−2.013 901 415 453 793(7)
$7\,^1D$	−2.010 210 028 457 978(11)	$7\,^3D$	−2.010 212 105 955 595(3)
$8\,^1D$	−2.007 816 512 563 811(6)	$8\,^3D$	−2.007 817 934 711 706(3)
$9\,^1D$	−2.006 175 671 437 641(7)	$9\,^3D$	−2.006 176 684 884 697(3)
$10\,^1D$	−2.005 002 071 654 250(6)	$10\,^3D$	−2.005 002 818 080 233(10)
$4\,^1F$	−2.031 255 144 381 749 6(17)	$4\,^3F$	−2.031 255 168 403 245 6(7)
$5\,^1F$	−2.020 002 937 158 742 7(5)	$5\,^3F$	−2.020 002 957 377 369 4(5)
$6\,^1F$	−2.013 890 683 815 549 7(4)	$6\,^3F$	−2.013 890 698 348 532 0(2)
$7\,^1F$	−2.010 205 248 074 011 7(3)	$7\,^3F$	−2.010 205 258 374 864 2(1)
$8\,^1F$	−2.007 813 297 115 014 1(6)	$8\,^3F$	−2.007 813 304 535 090 8(4)
$9\,^1F$	−2.006 173 406 897 324 6(8)	$9\,^3F$	−2.006173 412 365 043 0(7)
$10\,^1F$	−2.005 000 417 564 669 0(17)	$10\,^3F$	−2.005 000 421 686 604 0(11)
$11\,^1F$	−2.004 132 547 315 1300(38)	$11\,^3F$	−2.004 132 550 488 506 7(35)

[a]Numbers in parentheses indicate the uncertainties in the final one or two figures quoted.

TABLE III. Comparison of the T_n fit [Eq. (55)] to the variational eigenvalues of helium with the asymptotic coefficients from Table I (in 10^{-6} a.u.). The Ritz value is $a_4=3a_3^2/2$.

States	Coef.	Variational	Asymptotic	Ritz	Ritz defect
$n\,^3P$	a_3	68 295.8239(13)			
	a_4	6 927.23(3)		6996.47	69.24(3)
$n\,^1P$	a_3	−12 115.1027(17)			
	a_4	248.49(4)		220.16	28.33(4)
$n\,^3D$	a_3	2 880.4734(4)	2320(415)		
	a_4	13.761(11)	10(5)	12.446	1.315(11)
	a_5	−6 380.93(12)	−3745(1800)		
$n\,^1D$	a_3	2 101.8984(4)	2320(415)		
	a_4	5.987(11)	10(5)	6.627	−0.640(11)
	a_5	−3 076.50(12)	−3745(1800)		
$n\,^3F$	a_3	439.0430(6)	439(8)		
	a_4	0.330(22)	0.299(20)	0.283	0.047(22)
	a_5	−1 739.9(3)	−1719(72)		
$n\,^1F$	a_3	434.3202(7)	439(8)		
	a_4	0.329(24)	0.299(20)	0.283	0.046(24)
	a_5	−1 678.2(3)	−1719(72)		

potential is no longer of use due to large core penetration effects. The coefficient a_3 even becomes negative for the $n\,^1P$ states. Despite this, the Ritz estimate of a_4 remains remarkably accurate when applied *separately* to the ^1P and ^3P states, giving relatively small Ritz defects. However, the Ritz relation (22) becomes strongly violated if a singlet-triplet average of the variational eigenvalues is first formed, and the Ritz defect rises dramatically. The numerical values are $a_{4,\text{variational}}=3587.86(4)\times10^{-6}$ a.u. and $a_{4,\text{Ritz}}=1183.60\times10^{-6}$ a.u., for a Ritz defect of $2404.26(4)\times10^{-6}$ a.u. The Ritz expansion will clearly be much more successful if the singlet-triplet average is not performed.

Table IV compares the results using the T_n, T_n', and T_n'' functional forms for the quantum defect expansion. The quantity χ measures the goodness of fit (in the χ^2 sense [30]), normalized to unity for an adequate fit. The uncertainties in the fitting coefficients were estimated both from the statistics of the least-squares fit [30] and by actually varying the input data up and down by the amount of their uncertainties. Both methods gave about the same results. Although some of the χ values appear to be rather large, the fits are still extremely good by usual standards. For example, the largest deviation from the data listed in Table II for the T_n fit to the $n\,^3P$ states is only 242 kHz at $n=5$. The largest deviations become much less for the higher L states. The T_n' and T_n'' fits are true quantum-defect expansions in that n^* is determined by solving iteratively the equation

$$n^*=n-\delta_0-\delta_1/n^*-\delta_2/n^{*2}-\cdots \tag{58}$$

for a given set of the δ_i coefficients, and then iterating the least-squares fit for the δ_i to convergence. The iteration automatically takes into account the expansion of the denominators discussed in Secs. II and III. Approximating the denominators by, for example, $n^*\simeq n-\delta_0$ causes a remarkable deterioration of the accuracy of the fits by several orders of magnitude in the case of T_n'', and leads to unphysically large values for the higher-order coefficients. The T_n' fits are only slightly affected. For the D and F states, the δ_{10} term in T_n'' is not included in the fits because it does not produce a further improvement in the quality as measured by χ, and the values of δ_{10} are statistically consistent with zero.

At first sight, the T_n'' fits appear to be clearly superior (as measured by χ), especially for the P states. However, close examination reveals subtle problems related to the Ritz defect. First, the values of δ_0 are not consistent with the values obtained from T_n and T_n'. The differences are much larger than the apparent uncertainties. The reason is that accuracy estimates for the coefficients in a least-squares fit are not reliable if the functional form is not correct. The high *even* powers of $1/n^*$ in T_n'' give it an important functional flexibility in fitting the low-n data, but the absence of the δ_1/n^* term becomes relatively more serious in fitting the higher-n data where the value of δ_0 is most strongly determined. Second, T_n'' seriously overestimates the accuracy of extrapolated term energies. For intermediate n ($n<100$), the error in T_n' is dominated by the term δ_1/n^*, while the error in T_n'' decreases more rapidly as δ_2/n^{*2}. However, this more rapid decrease is not real—it is a consequence of not including the Ritz defect in T_n''. Notice that the values of δ_1 in T_n' are approximately equal to the Ritz defects listed in Table III.

The T_n'' form has long been used to provide a compact and accurate representation of atomic term values. However, the T_n' form rapidly improves in accuracy with increasing L. The above results suggest that if the accuracy of the data is sufficient to reveal a statistically significant

TABLE IV. Comparison of $1/n$ and quantum-defect fits to the nonrelativistic eigenvalues of helium. T_n' includes all powers of $1/n^*$ and T_n'' contains *even* powers only (the Ritz expansion) (in 10^{-6} a.u.).

States	Coef.	T_n fit [Eq. (55)]	Coef.	T_n' fit [Eq. (56)]	Coef.	T_n'' fit [Eq. (57)]
$n\,^3P$	a_3	68 295.9239(13)	δ_0	68 295.4521(12)	δ_0	68 293.614 29(10)
	a_4	6 927.23(3)	δ_1	−56.37(3)	δ_2	−18 636.068(13)
	a_5	−17 158.9(3)	δ_2	−17 958.93(27)	δ_4	−12 316.3(6)
	a_6	−11 412.2(1.3)	δ_3	−4 041.9(1.2)	δ_6	−8 080(9)
	a_7	2 353.1(2.7)	δ_4	122.4(2.3)	δ_8	−4 469(61)
	a_8	−28 055.0(2.0)	δ_5	−17 966.5(1.7)	δ_{10}	−2 017(125)
	χ	3 357	χ	3 103	χ	5.7
$n\,^1P$	a_3	−12 115.1027(17)	δ_0	−12 114.8601(17)	δ_0	−12 114.192 00(14)
	a_4	248.49(4)	δ_1	21.02(4)	δ_2	7 507.874(19)
	a_5	7 157.8(4)	δ_2	7 247.4(4)	δ_4	13 959.7(8)
	a_6	1 656.7(1.7)	δ_3	1 619.4(1.7)	δ_6	4 868(14)
	a_7	7 306(3)	δ_4	8 676(4)	δ_8	967(99)
	a_8	9 037.3(2.6)	δ_5	8 429.8(2.7)	δ_{10}	565(215)
	χ	860	χ	595	χ	2.9
$n\,^3D$	a_3	2 880.4734(4)	δ_0	2 880.4727(4)	δ_0	2 880.509 901(8)
	a_4	13.761(11)	δ_1	1.341(11)	δ_2	−6 351.8977(10)
	a_5	−6 380.93(12)	δ_2	−6 381.31(12)	δ_4	335.98(4)
	a_6	50.3(6)	δ_3	144.1(6)	δ_6	840.5(6)
	a_7	−232.4(1.6)	δ_4	−238.2(1.6)	δ_8	380.4(2.8)
	a_8	1 285.9(1.6)	δ_5	1 144.5(1.6)	δ_{10}	
	χ	33	χ	13	χ	0.64
$n\,^1D$	a_3	2 101.8984(4)	δ_0	2 101.8983(4)	δ_0	2 101.880 697(8)
	a_4	5.987(11)	δ_1	−0.636(11)	δ_2	−3 085.780 7(10)
	a_5	−3 076.50(12)	δ_2	−3 076.58(12)	δ_4	9.25(4)
	a_6	−100.7(6)	δ_3	−67.8(6)	δ_6	−320.1(6)
	a_7	276.0(1.6)	δ_4	274.5(1.6)	δ_8	−311.0(2.8)
	a_8	−474.3(1.6)	δ_5	−504.6(1.6)	δ_{10}	
	χ	24	χ	8.3	χ	1.1
$n\,^3F$	a_3	439.0430(6)	δ_0	439.0430(6)	δ_0	439.044 111(11)
	a_4	0.330(22)	δ_1	0.041(22)	δ_2	−1739.328 4(21)
	a_5	−1739.9(3)	δ_2	−1739.9(3)	δ_4	105.43(12)
	a_6	0.6(1.9)	δ_3	4.5(1.9)	δ_6	27.4(2.8)
	a_7	88(6)	δ_4	88(6)	δ_8	1.7(21.4)
	a_8	46(8)	δ_5	36(8)	δ_{10}	
	χ	83	χ	43	χ	5.1
$n\,^1F$	a_3	434.3202(7)	δ_0	434.3202(7)	δ_0	434.321 410(12)
	a_4	0.329(24)	δ_1	0.046(24)	δ_2	−1677.464 4(23)
	a_5	−1678.2(3)	δ_2	−1678.2(3)	δ_4	−68.66(13)
	a_6	1.8(2.1)	δ_3	5.4(2.1)	δ_6	18(3)
	a_7	−91(7)	δ_4	−91(7)	δ_8	77.5(23.6)
	a_8	51(8)	δ_5	41(8)	δ_{10}	
	χ	6.9	χ	0.60	χ	2.8

Ritz defect, then the T_n' form should be used, especially for purposes of extrapolating the term energies to higher n. This point should always be checked before adopting the Ritz expansion as a suitable functional form. The remarkable thing is that the Ritz expansion works so well. It is only the very high precision of the variational eigenvalues that makes the Ritz defect significant.

B. Alkali-metal quantum defects and polarizabilities

As a final application of the results of this paper, we examine the effect of the second-order dipole polarization correction $E^{(2)}$ on polarizabilities extracted from the quantum defects of the alkali metals. Since $E^{(2)}$ grows in proportion to α_1^2, it becomes much more important for these atoms. Keeping only terms up to $\langle r^{-6}\rangle$ and neglecting relativistic corrections, core penetration effects, etc., δ_0 can be written in the form

$$\delta_0(D\text{ states})=\frac{\alpha_1}{105}+\frac{\alpha_2-6\beta_1}{324}+\frac{10\,127\alpha_1^2}{12[(3)(5)(7)]^3}\,, \qquad (59)$$

$$\delta_0(F\text{ states})=\frac{\alpha_1}{630}+\frac{\alpha_2-6\beta_1}{17\,820}+\frac{941\,69\alpha_1^2}{352[(5)(7)(9)]^3}\,, \qquad (60)$$

$$\delta_0(G\text{ states})=\frac{\alpha_1}{2310}+\frac{\alpha_2-6\beta_1}{231\,660}+\frac{7\,461\,549\alpha_1^2}{520\,000[(7)(9)(11)]^3}\,. \tag{61}$$

Similar equations for higher L can be immediately written down using Eqs. (17) and (41). Assuming that δ_0 and the small correction term $\alpha_2-6\beta_1$ are known, the above are quadratic equations that can be solved for α_1. A summary of experimental values of δ_0 in the alkali metals has been given by Lorenzen and Niemax [9]. More accurate values for the cesium *S, P, D, F,* and *G* states have been obtained by Weber and Sansonetti [31], who also point out significant systematic errors in the quantum defect fits obtained in Ref. [9]. Values for α_1 and α_2 calculated in the relativistic random phase approximation (RRPA) have been tabulated by Johnson, Kolb, and Huang [28]. For Li^+ the nonadiabatic correction factor β_1 is $0.035\,26a_0^4/e^2$ [32]. For Na^+ and K^+, values of β_1 have been estimated by Eissa and Öpik [33] from oscillator strength sum rules, using the method of Dalgarno and Kingston [34]. In this method, the input data are $S(-1)=\langle(\sum_i \mathbf{r}_i)^2\rangle/3$ and $S(-2)=\alpha_1/4$, where $S(k)$ is the usual energy-weighted oscillator strength sum and the expectation value is with respect to the closed-shell ground state. These are used to calculate the constants a and b in the extrapolation formula [34]

$$S(k)=\left[\Delta E+\frac{a}{2.5-k}+\frac{b}{(2.5-k)^2}\right]^k S(0)\,, \tag{62}$$

where $S(0)$ is the number of electrons and ΔE is the smallest excitation energy (in Rydbergs) which contributes to the oscillator strength sums. Then $S(-3)=\beta_1/4$.

The required input values of $S(-1)$ for the alkali-metal ions were estimated by scaling the isoelectronic "experimental" inert gas values derived by Dalgarno and Kingston [34] (their Table 3) according to

$$S(-1)_{\text{alkali-metal ion}}=S(-1)_{\text{inert gas}}[\chi_m(\text{alkali-metal ion})/\chi_m(\text{inert gas})]\,, \tag{63}$$

where χ_m, the diamagnetic susceptibility, is proportional to the closely related quantity $\langle\sum_i r_i^2\rangle$. Using the Hartree-Fock values for χ_m [35] and the polarizabilities in Table V, this procedure, together with Eq. (62), yields essentially the exact β_1 for Li^+ ($\pm0.2\%$), and it reproduces the estimates of Eissa and Öpik [33] for Na^+ and K^+ to within 5% (when their older polarizabilities are used). The scaling factor in Eq. (63) ranges from 0.3776 for Li^+ to 0.8386 for Cs^+. The final results for β_1 are listed in Table V. The accuracy is adequate for purposes of the illustration to follow.

To illustrate the influence of the quadratic term in α_1 in Eqs. (59)–(61), Table V shows the values of δ_0 calculated with and without this term included [called δ_0 (quad.) and δ_0 (linear), respectively]. The effect is particularly large for the *D* states, where core penetration and exchange effects are also large [36]. In the case of Cs, the quadratic term increases δ_0 by about 70% to 0.442, but this is still much less than the observed value of 2.4663... due to core penetration. The *G* states of Cs are particularly interesting because core penetration and exchange effects become small. Estimates of these effects have been calculated by Sansonetti, Andrew, and Verges [36]. Extracting the coefficient of the leading $1/n^3$ term from

TABLE V. Comparison of quantum defects for the alkali metals calculated from Eqs. (59)–(61) with the experimental values. δ_0(quad.) includes the term quadradic in the polarizability while δ_0(linear) does not. All quantities are in atomic units.

States	α_1[a]	α_2[a]	β_1	δ_0(linear)	δ_0(quad.)	δ_0(expt.)[b]
Li ^2D	0.1894[c]	0.112	0.03526[d]	0.001 497	0.001 523	0.002 129
Na ^2D	0.9457	1.521	0.206[e]	0.009 89	0.010 54	0.015 543
Na ^2F	0.9457	1.521	0.206[e]	0.001 517	0.001 525	0.001 453
K ^2D	5.457	16.27	2.39[e]	0.057 9	0.079 6	0.277 0
K ^2F	5.457	16.27	2.39[e]	0.008 770	0.009 025	0.010 10
Rb ^2D	9.076	35.41	4.40[e]	0.114 2	0.174 3	1.347 16
Rb ^2F	9.076	35.41	4.40[e]	0.014 91	0.015 62	0.016 31
Cs ^2D	15.81	86.4	8.50[e]	0.259 8	0.442 1	2.466 315[f]
Cs ^2F	15.81	86.4	8.50[e]	0.027 08	0.029 22	0.033 414[f]
Cs ^2G	15.81	86.4	8.50[e]	0.006 997	0.007 105	0.007 039[f]

[a]RRPA results from Johnson, Kolb, and Huang (Ref. [28]).
[b]Lorenzen and Niemax (Ref. [9]), except as noted.
[c]The nonrelativistic variational value for α_1 is $0.1924a_0^3$ (Ref. [32]).
[d]Drake (Ref. [32]).
[e]Oscillator strength sum rule extrapolation (see text).
[f]Weber and Sansonetti (Ref. [31]).

their results, the contribution to δ_0 is 0.000 026 to give a corrected quantum defect of 0.007 013 for the G states. Using the corrected value in Eq. (61) and solving for α_1 yields $\alpha_1 = 15.61 a_0^3$. This is somewhat smaller than the RRPA value of $15.81 a_0^3$, but within the range of probable accuracy. It is also smaller than the value $15.770(3) a_0^3$ obtained by Weber and Sansonetti [31], who did not include the quadratic term in their fit to the measured frequencies. The quadratic term accounts for most of the difference. For the F states, the corresponding penetration and exchange correction [36] to δ_0 is 0.007 88. This is the same order of magnitude as the difference between the calculated and measured values shown in Table V. However, Eqs. (59)–(61) are based on just the leading two terms in the asymptotic potential, together with the quadratic term. For the F states, and possibly also for the G states, the leading two terms may not be sufficient at this level of accuracy.

V. DISCUSSION

The central result of this paper is the general expression (41) for the second-order dipole polarization correction $E^{(2)}$. The coefficients of the even powers of $1/n$ have been shown to be in accord with what one would expect from quantum-defect theory, using the Ritz expansion for the quantum defect. In fact Hartree's proof that the Ritz expansion is an exact analytic result for local central potentials provides a powerful method for finding at least the *even* terms in a $1/n$ expansion for the second-order energy resulting from any short-range perturbation. For example, the same techniques could be applied to the $1/r^6$ term in the asymptotic potential.

The exact effective potential experienced by the Rydberg electron is known to be nonlocal and energy dependent because of short-range and exchange effects. In this case, one would expect to see deviations from the Ritz expansion as an exact functional form for the n dependence of Rydberg energies. A $1/n$ expansion fit to high precision variational eigenvalues in fact shows a well-defined "Ritz defect," which represents the degree to which the Ritz expansion for the quantum defect is not valid. In this case, the odd as well as the even powers of $1/n^*$ should be included in the quantum-defect expansion. The lowest-order Ritz defect then reappears as the coefficient of $1/n^*$. A particularly important point is that unless this term is known to vanish, it dominates the error of extrapolations of Rydberg energies up to moderately high values of n. Omitting it gives unrealistically small error estimates, even though a fit to the data may appear to be quite adequate. It is also important to bear in mind that the quality of the fit improves dramatically if a full iterative definition of the quantum defect is used. This implicitly takes into account the quantum-defect expansion in the denominators of Eq. (2).

The final conclusion of this paper is that the second-order polarization energy has a significant effect on polarizabilities extracted from experimental quantum defects. The results of Table V show that the accuracy of polarizabilities obtained in this way rapidly improves with increasing L. The G state result for Cs is particularly accurate, and provides an important test of calculations. However, a complete reanalysis of the experimental data with the quadratic term included would be desirable.

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