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Asymptotic expansion for δ -function matrix elements of helium

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This paper extends the methods of asymptotic analysis extensively developed for energy-level calculations of Rydberg states to the evaluation of matrix elements of $\delta(\mathbf{r})$. All terms up to x^{-8} in the asymptotic potential are systematically derived from a simple perturbation expansion. The formalism is developed in a way that closely parallels that for the corresponding energy expansion. The results are comparable in accuracy to the energy itself. Detailed numerical comparisons with high-precision variational calculations are presented for the states of helium up to $nL = 10K$ (i.e., $L = 7$). For $L \geq 5$, the accuracy of the asymptotic expansion exceeds what has been achieved variationally. The asymptotic expansion for the specific mass correction to $\langle \delta(\mathbf{r}) \rangle$ is also obtained. Here the accuracy rivals the variational results even for $L = 3$. Similar methods can be applied to the calculation of a wide variety of other atomic properties.

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I. INTRODUCTION

Expectation values of the Dirac δ function play an important role in the calculation of many atomic properties such as relativistic corrections, hyperfine structure, quantum electrodynamic, and weak-interaction effects [1,2]. For hydrogenic atoms, the nonrelativistic expectation value is simply

$$\langle nl|\delta(\mathbf{r})|nl\rangle = \frac{Z^3}{\pi n^3 a_\mu^3}, \quad (1)$$

where $a_\mu = (m/\mu)a_0$ is the reduced-mass Bohr radius and $\mu = mM/(m+M)$ is the reduced electron mass. However, for atoms containing more than one electron, accurate values of $\langle \delta(\mathbf{r}) \rangle$ (or, more generally, the electron density near the nucleus) are notoriously difficult to obtain [3]. Variational calculations that optimize the energy are not particularly sensitive to this part of configuration space. In fact, it is the uncertainty in $\langle \delta(\mathbf{r}) \rangle$ that ultimately limits the accuracy of recent high-precision variational calculations [4-6] through its effect on the term $\alpha^2 Z[\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)]$ in the Breit interaction. Matrix-element identities that replace $\langle \delta(\mathbf{r}) \rangle$ by the expectation value of a global operator [2,7,8] offer some improvement in accuracy [9], but not sufficient to overcome the above limitation.

For low-lying states, there is no substitute for direct high-precision calculations of the wave function near the origin. However, for high- nL Rydberg states, powerful asymptotic-expansion methods are available [10-12]. In the past, these have been applied primarily to the calculation of energy levels. The results to be presented here show that values of $\langle \delta(\mathbf{r}) \rangle$ comparable in accuracy to the total energy itself can be obtained by relatively simple means. Section II presents the asymptotic-expansion method in a somewhat different form from that used in the past [11], and then extends it to the calculation of $\langle \delta(\mathbf{r}) \rangle$. Finite-nuclear-mass corrections are also dis-

cussed. Section III compares the results with high-precision variational calculations for the Rydberg states of helium. The comparisons show that the accuracy of the asymptotic-expansion method for $\langle \delta(\mathbf{r}) \rangle$ rapidly improves in accuracy with increasing L , and ultimately exceeds what has been achieved variationally. The asymptotic-expansion values for the specific nuclear-mass corrections to $\langle \delta(\mathbf{r}) \rangle$ are more accurate even for G states.

II. ASYMPTOTIC-EXPANSION THEORY

A. Basic formalism

The purpose of this section is to develop a basic formalism for performing asymptotic expansions. Although many of the results have been obtained before [10,11], it seems worthwhile to review this material in a systematic way that is well suited to calculations of both the energy and other atomic properties such as $\langle \delta(\mathbf{r}) \rangle$. It will turn out that there are close parallels between the two.

For a sufficiently high- nL Rydberg state of helium, core penetration and exchange effects of the outer electron with the core $1s$ electron become negligible. Under these circumstances, the usual procedure is to introduce a Feshbach projection operator $P = |1s\rangle\langle 1s|$ and expand the optical potential for the Rydberg electron in powers of the perturbing potential. This clearly establishes the connection with scattering theory [13]. The approach used here is based instead on a simple perturbation expansion for the total wave function. The results for the total energy are the same in the end, but the formalism is better adapted to the calculation of quantities other than the energy.

The starting point is to write the total Hamiltonian for helium in the form (atomic units are used throughout)

$$H(\mathbf{r}, \mathbf{x}) = H_0(\mathbf{r}, \mathbf{x}) + V, \quad (2)$$

where

$$H_0(\mathbf{r}, \mathbf{x}) = -\frac{1}{2}\nabla_r^2 - \frac{Z}{r} - \frac{1}{2}\nabla_x^2 - \frac{Z-1}{x}$$

$$= h_0(\mathbf{r}, Z) + h_0(\mathbf{x}, Z-1) \quad (3)$$

and

$$V = \frac{1}{|\mathbf{r}-\mathbf{x}|} - \frac{1}{x} \quad (4)$$

assuming infinite nuclear mass. Mass-polarization effects resulting from the term $-(\mu/M)\nabla_r \cdot \nabla_x$ can easily be taken into account at the end by transforming to Jacobi coordinates [14]. In the above, \mathbf{r} denotes the position vector of the inner electron and \mathbf{x} the position vector of the Rydberg electron. As usual, exchange effects will be ignored and the electrons treated as distinguishable. For $r < x$, the potential has the well-known multipole expansion

$$V = \frac{1}{x} \sum_{l=1}^{\infty} \left(\frac{r}{x} \right)^l P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}}). \quad (5)$$

The solutions to the full Schrödinger equation

$$H(\mathbf{r}, \mathbf{x})\Psi(\mathbf{r}, \mathbf{x}) = E\Psi(\mathbf{r}, \mathbf{x}) \quad (6)$$

will now be expanded as a perturbation series with V as the perturbation according to

$$\Psi(\mathbf{r}, \mathbf{x}) = \Psi_0(\mathbf{r}, \mathbf{x}) + \Psi_1(\mathbf{r}, \mathbf{x}) + \dots, \quad (7a)$$

$$E = E_0 + E_1 + \dots, \quad (7b)$$

where

$$(H_0 - E_0)\Psi_0 = 0 \quad (8)$$

is the zero-order equation and, for the j th perturbation equation,

$$(H_0 - E_0)\Psi_j + V\Psi_{j-1} = \sum_{k=1}^j E_k \Psi_{k-j}. \quad (9)$$

With the assumed normalization $\langle \Psi_j | \Psi_0 \rangle = 0$ for $j \geq 1$, it follows from (9) that

$$E_j = \langle \Psi_0 | V | \Psi_{j-1} \rangle. \quad (10)$$

The solution to the zero-order equation (8) will be written in the form

$$\Psi_0(\mathbf{r}, \mathbf{x}) = \varphi_{1s}(\mathbf{r})\chi_{nL}(\mathbf{x})$$

$$\equiv \varphi_0(\mathbf{r})\chi_0(\mathbf{x}), \quad (11)$$

with

$$E_0 = \mathcal{E}_0 + e_0$$

$$= -\frac{Z^2}{2} - \frac{(Z-1)^2}{2n^2}. \quad (12)$$

A subscript "0" will be used throughout to denote the unperturbed initial state.

A convenient way of enumerating the contributions to the perturbed wave functions is to write them out in terms of their spectral representations according to

$$|\Psi_1\rangle = \sum_m \frac{V_{0,m}|m\rangle}{\Delta_m}, \quad (13)$$

$$|\Psi_2\rangle = \sum_{m,n} \frac{V_{0,m}V_{m,n}|n\rangle}{\Delta_m\Delta_n}, \quad (14)$$

$$|\Psi_3\rangle = \sum_{m,n} \frac{V_{0,m}V_{m,n}V_{n,p}|p\rangle}{\Delta_m\Delta_n\Delta_p} - E_2 \sum_m \frac{V_{0,m}|m\rangle}{\Delta_m^2}, \quad (15)$$

$$|\Psi_4\rangle = \sum_{m,n} \frac{V_{0,m}V_{m,n}V_{n,p}V_{p,q}|q\rangle}{\Delta_m\Delta_n\Delta_p\Delta_q}$$

$$- E_2 \sum_{m,n} V_{0,m}V_{m,n} \left[\frac{1}{\Delta_m^2\Delta_n} + \frac{1}{\Delta_m\Delta_n^2} \right] |n\rangle$$

$$- E_3 \sum_m \frac{V_{0,m}|m\rangle}{\Delta_m^2}. \quad (16)$$

Here, the summation indices m, n, \dots are a shorthand notation for two complete sets of quantum numbers $(m, m'), (n, n'), \dots$ for the two electrons, and the sums are over all single and double excitations, including integrations over the continua. The $V_{m,n}$ denote complete two-particle matrix elements. The denominators are the excitation energies given by

$$\Delta_m = D_m + d_{m'}, \quad (17)$$

with

$$\Delta_m = \mathcal{E}_0 - \mathcal{E}_m, \quad (18)$$

$$d_{m'} = e_0 - e_{m'}. \quad (19)$$

As will be seen below, intermediate states where the inner electron returns to the $1s$ state have a special significance. These states will be distinguished by adding a subscript "0" to the summation index, for example, m_0 . Then $D_{m_0} = 0$ and

$$\Delta_{m_0} = d_{m'}. \quad (20)$$

Since the initial $1s$ state is spherically symmetric and the monopole term is absent from Eq. (5), it follows that $V_{0,m_0} = 0$ and $V_{m_0,n_0} = 0$ for all m and n . This constrains the terms that can appear in the $|\Psi_j\rangle$ according to the following selection rules: (i) The leading Δ_m in the denominator cannot be Δ_{m_0} . (ii) Two adjacent factors such as $\Delta_n\Delta_p$ cannot be $\Delta_{n_0}\Delta_{p_0}$.

The adiabatic approximation and the summation rules for the evaluation of the matrix-element products in the numerators of the $|\Psi_i\rangle$ lead to important further simplifications. These will be discussed next. The adiabatic approximation consists of assuming that $d_{m'} \ll D_m$ for $m \neq m_0$ and expanding

$$\frac{1}{\Delta_m} = \frac{1}{D_m} \left[1 - \frac{d_{m'}}{\Delta_m} + \frac{d_{m'}^2}{\Delta_m^2} - \dots \right]. \quad (21)$$

The leading term is the adiabatic approximation and the higher-order terms are nonadiabatic corrections. We will focus here primarily on the adiabatic terms. The nonadiabatic corrections can be added at the end by the use of

commutator relations as thoroughly discussed by Drachman [11].

The matrix-element summations can be simplified as follows. Since the wave functions for the initial state and all intermediate states have a simple product form

$$\Psi_m(\mathbf{r}, \mathbf{x}) = \varphi_m(\mathbf{r})\chi_{m'}(\mathbf{x}), \quad (22)$$

the matrix elements $V_{m,n}$ similarly factorize for each multipole

$$V^{(l)} = \frac{r^l}{x^{l+1}} P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}}) \quad (23)$$

according to

$$V_{m,n}^{(l)} = \sum_{\mu} U_{m,n}^{(l,\mu)} u_{m',n'}^{(l,\mu)}, \quad (24)$$

where

$$U_{m,n}^{(l,\mu)} = \left[\frac{4\pi}{2l+1} \right]^{1/2} \langle \varphi_m | r^l Y_l^\mu(\hat{\mathbf{r}}) | \varphi_n \rangle, \quad (25)$$

$$u_{m',n'}^{(l,\mu)} = \left[\frac{4\pi}{2l+1} \right]^{1/2} \langle \chi_{m'} | x^{-l-l'} Y_l^{\mu*}(\hat{\mathbf{x}}) | \chi_{n'} \rangle, \quad (26)$$

and the spherical-harmonic addition theorem has been used. A further simplification occurs in expressions for scalar quantities such as E_2 , which we now consider as an example. In the adiabatic approximation, the l th multipole contribution is

$$\begin{aligned} E_2^{(l)} &= \sum_m \frac{V_{0,m}^{(l)} V_{m,0}^{(l)}}{D_m} \\ &= \sum_m \frac{U_{0,m}^{(l,\mu)} U_{m,0}^{(l,\mu')}}{D_m} \sum_{\mu, \mu'} u_{0,m'}^{(l,\mu)} u_{m',0}^{(l,\mu')}. \end{aligned} \quad (27)$$

The last summation over m' can be completed by closure with the result

$$\begin{aligned} \sum_{m'} u_{0,m'}^{(l,\mu)} u_{m',0}^{(l,\mu')} &= \langle \chi_0 | x^{-2l-2} Y_l^\mu(\hat{\mathbf{x}}) Y_l^{\mu'}(\hat{\mathbf{x}}) | \chi_0 \rangle \\ &= (-1)^\mu \delta_{\mu, -\mu'} \langle \chi_0 | x^{-2l-2} | Y_l^\mu(\hat{\mathbf{x}}) |^2 | \chi_0 \rangle. \end{aligned} \quad (28)$$

Thus

$$\begin{aligned} E_2^{(l)} &= \sum_{m,\mu} \left[(-1)^\mu \frac{U_{0,m}^{(l,\mu)} U_{m,0}^{(l,-\mu)}}{D_m} \right] \\ &\quad \times \langle \chi_0 | x^{-2l-2} | Y_l^\mu(\hat{\mathbf{x}}) |^2 | \chi_0 \rangle. \end{aligned} \quad (29)$$

The quantity in the large parentheses is independent of μ after summing over magnetic quantum numbers for the intermediate states, and so we can set $\mu=0$ there. Then, using

$$\begin{aligned} |\Psi_4\rangle &= \sum_{m,n} \frac{V_{0,m} V_{m,n} V_{n,p} V_{p,q}}{D_m D_n D_p D_q} |q\rangle + \sum_{p,q} \frac{\langle \varphi_0 \chi_0^{(1)} | V | p \rangle V_{p,q}}{D_p D_q} |q\rangle + \sum_q \frac{\langle \varphi_0 \chi_0^{(1')} | V | q \rangle |q\rangle}{D_q} + |\varphi_0 \chi_0^{(1'')} \rangle + |\varphi_0 \chi_0^{(2)} \rangle \\ &\quad - E_2 \sum_{m,n} V_{0,m} V_{m,n} \left[\frac{1}{D_m^2 D_n} + \frac{1}{D_m D_n^2} \right] |n\rangle - \langle x^{-4} \rangle \beta_1 |\varphi_0 \chi_0^{(1)} \rangle - E_2 |\varphi_0 \tilde{\chi}_0^{(1)} \rangle - E_3 \sum_m \frac{V_{0,m} |m\rangle}{D_m^2}, \end{aligned} \quad (39)$$

$$\sum_{\mu} |Y_l^\mu(\hat{\mathbf{x}})|^2 = \frac{2l+1}{4\pi} \quad (30)$$

in the second factor, the final result is

$$E_2^{(l)} = -\frac{1}{2} \alpha_l \langle \chi_0 | x^{-2l-2} | \chi_0 \rangle, \quad (31)$$

where

$$\alpha_l = -2 \sum_m \frac{U_{0,m}^{(l)} U_{m,0}^{(l)}}{D_m} \quad (32)$$

is the 2^l -pole polarizability and

$$U_{0,m}^{(l)} = \langle \varphi_0 | r^l P_l(\cos\theta) | \varphi_m \rangle. \quad (33)$$

Proceeding in this way, the $|\Psi_j\rangle$ in the adiabatic approximation are

$$|\Psi_1\rangle = \sum_m \frac{V_{0,m} |m\rangle}{D_m}, \quad (34)$$

$$|\Psi_2\rangle = \sum_{m,n} \frac{V_{0,m} V_{m,n} |n\rangle}{D_m D_n} + |\varphi_0 \chi_0^{(1)} \rangle, \quad (35)$$

where

$$|\varphi_0 \chi_0^{(1)} \rangle = \sum_{m,n_0} \frac{V_{0,m} V_{m,n_0} |n_0\rangle}{D_m d_n} \quad (36a)$$

$$= -\frac{1}{2} \alpha_1 |\varphi_0 \rangle \sum_n \frac{\langle \chi_0 | x^{-4} | \chi_n \rangle | \chi_n \rangle}{d_n} \quad (36b)$$

in the dipole approximation. The technique for summing over m is the same as that leading to Eq. (31) for E_2 . The remaining sum over n defines the solution to the first-order perturbation equation

$$\left[h_0(\mathbf{x}, Z-1) + \frac{(Z-1)^2}{2n^2} \right] \chi_0^{(1)} - \frac{\alpha_1}{2x^4} \chi_0 = -\frac{\alpha_1}{2} \langle x^{-4} \rangle \chi_0, \quad (37)$$

which can be solved analytically [11,12,15]. Similarly

$$\begin{aligned} |\Psi_3\rangle &= \sum_{m,n} \frac{V_{0,m} V_{m,n} V_{n,p} |p\rangle}{D_m D_n D_p} + \sum_p \frac{\langle \varphi_0 \chi_0^{(1)} | V | p \rangle |p\rangle}{D_p} \\ &\quad + |\varphi_0 \chi_0^{(1')} \rangle - E_2 \sum_m \frac{V_{0,m} |m\rangle}{D_m^2}. \end{aligned} \quad (38)$$

The second term corresponds to the first term with $n=n_0$ (and so $D_n=d_n$), and the third term corresponds to the first term with $p=p_0$. $\chi_0^{(1')}$ satisfies a perturbation equation similar to Eq. (37), but with x^{-4} replaced by x^{-7} [see Eq. (44) below]. These are the only substitutions allowed by the selection rules for the numerators. Finally,

where

$$\beta_l = \sum_m \frac{U_{0,m}^{(l)} U_{m,0}^{(l)}}{D_m^2} \quad (40)$$

and

$$|\tilde{\chi}_0^{(1)}\rangle = -\frac{1}{2}\alpha_1 \sum_n \frac{\langle \chi_0 | x^{-4} | \chi_n \rangle | \chi_n \rangle}{d_n^2} \quad (41)$$

in the dipole approximation. The second, third, fourth, and fifth terms come from the replacements $n \rightarrow n_0$, $p \rightarrow p_0$, $q \rightarrow q_0$, and $(n, q) \rightarrow (n_0, q_0)$, respectively, in the first term. Thus $\chi_0^{(2)}$ satisfies a second-order perturbation equation analogous to Eq. (37), and $\chi_0^{(1)'}$ satisfies an x^{-8} first-order equation. The last two terms come from the replacement $p \rightarrow p_0$ in the two parts of the sixth term containing E_2 . All terms up to $|\Psi_4\rangle$ will be needed to determine $\langle \delta(\mathbf{r}_1) \rangle$ up to terms of order $\langle x^{-8} \rangle$, as discussed in Sec. II C. To this order, the $\chi_0^{(1)'}$, $\chi_0^{(1)''}$, and $\chi_0^{(2)}$ terms can be neglected. The $\tilde{\chi}_0^{(1)}$ term does not contribute because of orthogonality.

B. Energy expansion

It is now a straightforward matter to obtain the asymptotic energy expansion from Eq. (10). Using Eq. (31), E_2 contains the multipole terms

$$\begin{aligned} E_2 = & -\frac{1}{2}(\alpha_1 \langle x^{-4} \rangle + \alpha_2 \langle x^{-6} \rangle + \alpha_3 \langle x^{-8} \rangle + \dots) \\ & + 3\beta_1 \langle x^{-6} \rangle + \frac{15}{2}\beta_2 \langle x^{-8} \rangle \\ & + \gamma \left[\frac{8}{5} \langle x^{-7} \rangle - 36 \left[1 + \frac{L(L+1)}{10} \right] \langle x^{-8} \rangle \right] + \dots, \end{aligned} \quad (42)$$

where β_1 and β_2 are the dipole and quadrupole first-order nonadiabatic corrections, and γ is the second-order dipole nonadiabatic correction discussed by Drachman [11]. The expectation values are with respect to the Rydberg electron. The β_l are defined by Eq. (40) and

$$\gamma = -\frac{1}{2} \sum_m \frac{U_{0,m}^{(1)} U_{m,0}^{(1)}}{D_m^3}. \quad (43)$$

Next,

$$E_3 = \frac{1}{2} \delta \langle x^{-7} \rangle, \quad (44)$$

where

$$\delta = 2 \sum_{m,n} \sum_{l,l'=1}^2 \frac{U_{0,m}^{(l)} U_{m,n}^{(4-l-l')} U_{n,0}^{(l')}}{D_m D_n}. \quad (45)$$

Finally,

$$\begin{aligned} E = & E_2 + E_3 + E_4 + (\Delta E_4)_{\text{nonad}} \\ = & -\frac{1}{2}\alpha_1 \langle x^{-4} \rangle + \frac{1}{2}(-\alpha_2 + 6\beta_1) \langle x^{-6} \rangle + \frac{1}{2}(\delta + \frac{16}{5}\gamma) \langle x^{-7} \rangle \\ & + \frac{1}{2} \left[-\alpha_3 + 15\beta_2 - \epsilon + \alpha_1\beta_1 - 72\gamma \left[1 + \frac{L(L+1)}{10} \right] \right] \langle x^{-8} \rangle + e_0^{(2)}. \end{aligned} \quad (49)$$

TABLE I. Asymptotic expansion coefficients for the energy (ξ) and δ function ($\Delta\xi$). For each line, ξ stands for the coefficient in the first column.

Coeff. (ξ)	ξ	$\Delta\xi$	$\Delta\xi'$	$\Delta\xi''$
α_1	$\frac{9}{2Z^4}$	$\frac{31}{Z^6}$	$\frac{81}{4Z^6}$	$\frac{43}{4Z^6}$
α_2	$\frac{15}{Z^6}$	$\frac{557}{4Z^8}$	$\frac{225}{4Z^8}$	$\frac{107}{4Z^8}$
α_3	$\frac{525}{4Z^8}$	$\frac{6165}{4Z^{10}}$	$\frac{21\,315}{16Z^{10}}$	$\frac{3265}{16Z^{10}}$
β_1	$\frac{43}{8Z^6}$	$\frac{2561}{48Z^8}$	$\frac{1285}{48Z^8}$	$\frac{319}{12Z^8}$
β_2	$\frac{107}{8Z^8}$	$\frac{19\,097}{120Z^{10}}$	$\frac{8733}{80Z^{10}}$	$\frac{2399}{48Z^{10}}$
γ	$\frac{319}{48Z^8}$	$\frac{24\,619}{288Z^{10}}$	$\frac{20\,219}{576Z^{10}}$	$\frac{9673}{192Z^{10}}$
δ	$\frac{213}{2Z^8}$	$\frac{2587}{2Z^{10}}$	$\frac{6035}{2Z^{10}}$	$\frac{4313}{8Z^{10}}$
ϵ	$\frac{4329}{32Z^{10}}$	$\frac{243\,103}{128Z^{12}}$	$\frac{6397}{8Z^{12}}$	$\frac{140\,751}{128Z^{12}}$
$\Delta\tilde{\beta}'_1$	$\frac{771}{32Z^8}$			

$$E_4 = -\frac{1}{2}\epsilon \langle x^{-8} \rangle - \frac{1}{2}\alpha_1 \langle \chi_0^{(1)} | x^{-4} | \chi_0 \rangle + \frac{1}{2}\alpha_1\beta_1 \langle x^{-4} \rangle^2, \quad (46)$$

where

$$\epsilon = -2 \sum_{m,n} \sum_p \frac{U_{0,m}^{(1)} U_{m,n}^{(1)} U_{n,p}^{(1)} U_{p,0}^{(1)}}{D_m D_n D_p}. \quad (47)$$

The second term in E_4 is the second-order correction $e_0^{(2)}$ to the energy of the Rydberg electron due to the polarization of the core (which is itself a second-order effect). A general expression and analysis for this term has been given previously [15].

E_4 contains a term quadratic in $\langle x^{-4} \rangle$. However, as shown in the Appendix, the leading nonadiabatic correction to E_4 is

$$(\Delta E_4)_{\text{nonad}} = \frac{1}{2}\alpha_1\beta_1 (\langle x^{-8} \rangle - \langle x^{-4} \rangle^2). \quad (48)$$

The corresponding correction is effectively included in the term Δ_2 defined by Drachman [11]. This cancels the $\langle x^{-4} \rangle^2$ term to give the final result

The values of the coefficients are summarized in Table I. They agree with those tabulated by Drachman [11]. The above demonstrates the equivalence of the direct perturbation expansion to the optical-potential expansion used by Drachman.

C. δ -function expansion

The perturbation expansion for the asymptotic wave function obtained in Sec. II A now allows the expectation value of an operator W to be similarly calculated. An alternative procedure is to replace V by $V + W$ in calculating the energy, and retain all terms in the energy which are linear in W (the Hellman-Feynman theorem). This was the procedure used by Drachman [12] to obtain the leading relativistic correction. However, a complete enumeration of all the higher-order terms appears to be simpler, starting directly from the wave function as done here.

For simplicity, let W be a scalar single-particle operator. Retaining terms up to $\langle x^{-8} \rangle$, the expectation value of W is

$$\langle W \rangle = \frac{W_0 + W_1 + W_2 + W_3 + W_4}{1 + N_1 + N_2 + N_3 + N_4}, \quad (50)$$

where

$$W_0 = \langle \Psi_0 | W | \Psi_0 \rangle, \quad (51)$$

$$W_1 = 2 \langle \Psi_1 | W | \Psi_0 \rangle = 0, \quad (52)$$

$$W_2 = 2 \langle \Psi_2 | W | \Psi_0 \rangle + \langle \Psi_1 | W | \Psi_1 \rangle, \quad (53)$$

$$W_3 = 2 \langle \Psi_3 | W | \Psi_0 \rangle + 2 \langle \Psi_2 | W | \Psi_1 \rangle, \quad (54)$$

$$W_4 = 2 \langle \Psi_4 | W | \Psi_0 \rangle + 2 \langle \Psi_3 | W | \Psi_1 \rangle + \langle \Psi_2 | W | \Psi_2 \rangle, \quad (55)$$

and the N 's are the analogous overlap integrals obtained by setting $W = 1$. Then, expanding the denominator,

$$\langle W \rangle \simeq W_0(1 - N_2 - N_3 - N_4 + N_2^2) + W_2(1 - N_2) + W_3 + W_4. \quad (56)$$

There is a close parallel between the form of the final results for $\langle W \rangle$ and the corresponding terms in Eq. (49) for the energy (which reflects the Hellman-Feynman theorem). In fact, α_l , δ , and ϵ are systematically replaced by $\Delta\alpha_l$, $\Delta\delta$, and $\Delta\epsilon$ defined by

$$\Delta\alpha_l = \Delta\alpha'_l + \Delta\alpha''_l \quad (57)$$

and similarly for $\Delta\delta$ and $\Delta\epsilon$. The component parts for each are

$$\Delta\alpha'_l = -4 \sum_{m,n} \frac{U_{0,m}^{(l)} U_{m,n}^{(l)} W_{n,0}}{D_m D_n}, \quad (58)$$

$$\Delta\alpha''_l = 2W_0 \sum_m \frac{U_{0,m}^{(l)} U_{m,0}^{(l)}}{D_m^2} \equiv 2W_0\beta, \quad (59)$$

$$\Delta\delta' = 4 \sum_{m,n} \sum_{l,l'=1}^2 \frac{U_{0,m}^{(l)} U_{m,n}^{(4-l-l')} U_{n,p}^{(l')} W_{p,0}}{D_m D_n D_p}, \quad (60)$$

$$\Delta\delta'' = -2W_0 \sum_{m,n} \sum_{l,l'=1}^2 U_{0,m}^{(l)} U_{m,n}^{(4-l-l')} U_{n,0}^{(l')} \times \left[\frac{1}{D_m^2 D_n} + \frac{1}{D_m D_n^2} \right], \quad (61)$$

$$\Delta\epsilon' = -4 \sum_{m,n} \frac{U_{0,m}^{(1)} U_{m,n}^{(1)} U_{n,p}^{(1)} U_{p,q}^{(1)} W_{q,0}}{D_m D_n D_p D_q} - 2 \sum_{m,n} \frac{U_{0,m}^{(1)} U_{m,n}^{(1)} W_{n,p} U_{p,q}^{(1)} U_{q,0}^{(1)}}{D_m D_n D_p D_q}, \quad (62)$$

$$\Delta\epsilon'' = 2W_0 \sum_{m,n} \frac{U_{0,m}^{(1)} U_{m,n}^{(1)} U_{n,p}^{(1)} U_{p,0}^{(1)}}{D_m D_n D_p} \times \left[\frac{2}{D_m^2 D_n D_p} + \frac{1}{D_m D_n^2 D_p} \right]. \quad (63)$$

The replacements for the nonadiabatic correction terms β_l and γ are slightly different because of extra numerical factors which appear when Δ_m^2 in the denominator is expanded according to Eq. (21) to give Eq. (59) as the leading term. The nonadiabatic correction factors are

$$\Delta\beta'_l = 2 \sum_{m,n} \frac{U_{0,m}^{(l)} U_{m,n}^{(l)} W_{n,0}}{D_m^2 D_n}, \quad (64)$$

$$\Delta\beta''_l = -2W_0 \sum_m \frac{U_{0,m}^{(l)} U_{m,0}^{(l)}}{D_m^3} \equiv 4W_0\gamma_l, \quad (65)$$

and

$$\Delta\gamma' = - \sum_{m,n} \frac{U_{0,m}^{(l)} U_{m,n}^{(l)} W_{n,0}}{D_m^3 D_n}, \quad (66)$$

$$\Delta\gamma'' = \frac{3}{2} W_0 \sum_m \frac{U_{0,m}^{(l)} U_{m,0}^{(l)}}{D_m^4}, \quad (67)$$

where $\Delta\beta_l = \Delta\beta'_l + \Delta\beta''_l$ and $\Delta\gamma = \Delta\gamma' + \Delta\gamma''$. The extra numerical factors are $2/1!$ for $\Delta\beta'_l$ and $6/2! = 3$ for $\Delta\gamma''$. The quantity

$$\Delta\tilde{\beta}'_l = 2 \sum_{m,n} \frac{U_{0,m}^{(l)} U_{m,n}^{(l)} W_{n,0}}{D_m D_n^2} \quad (68)$$

will also be required. This does not appear directly as part of Eq. (64) for $\Delta\beta'_l$ because $[h_0(\hat{\mathbf{x}}, \mathbf{Z} - 1), W] = 0$. As a consequence, the corresponding nonadiabatic correction for the D_n term in the denominator of (58) does not contribute.

With the above definitions, the same summation techniques used for the energy expansion in Secs. II A and II B yield

$$W_0 N_2 = \frac{1}{2} \sum_l \Delta\alpha'_l \langle x^{-2l-2} \rangle, \quad (69)$$

$$W_0 N_3 = -\frac{1}{2} \Delta\delta'' \langle x^{-7} \rangle, \quad (70)$$

$$W_0 N_4 = \frac{1}{2}(\Delta\epsilon'' - \alpha_1 \Delta\beta_1') \langle x^{-8} \rangle + \Delta\alpha_1'' \langle \chi_0 | x^{-4} | \chi_0^{(1)} \rangle + W_0 \langle \chi_0^{(1)} | \chi_0^{(1)} \rangle, \quad (71)$$

and

$$W_0 N_2^2 = \frac{1}{2} \beta_1 \Delta\alpha_1'' \langle x^{-4} \rangle^2 \quad (72)$$

to sufficient accuracy. Similarly, from Eq. (53),

$$W_2 = -\frac{1}{2} \sum_l \Delta\alpha_l' \langle x^{-2l-2} \rangle + \langle \varphi_0 \chi_0^{(1)} | W | \varphi_0 \chi_0 \rangle + \langle \Psi_1 | W | \Psi_1 \rangle. \quad (73)$$

For simplicity of presentation, we now assume that W is the particular scalar operator

$$W = \frac{\pi a_0^3}{Z^3} \delta(\mathbf{r}) \quad (74)$$

so that $W_0 = 1$. The second term in W_2 above then vanishes because $\langle \chi_0^{(1)} | \chi_0 \rangle = 0$, and the third term vanishes because only s states contribute to $\langle \delta(\mathbf{r}) \rangle$. Continuing with this assumption,

$$W_3 = \frac{1}{2} \Delta\delta' \langle x^{-7} \rangle \quad (75)$$

and

$$W_4 = -\frac{1}{2} \Delta\epsilon' \langle x^{-8} \rangle + \frac{1}{2} \alpha_1 (\Delta\beta_1' + \Delta\bar{\beta}_1') \langle x^{-8} \rangle - \Delta\alpha_1' \langle \chi_0^{(1)} | x^{-4} | \chi_0 \rangle + W_0 \langle \chi_0^{(1)} | \chi_0^{(1)} \rangle. \quad (76)$$

The fourth (i.e., last) term of W_4 and one half of the third term come from the $\langle \Psi_2 | W | \Psi_2 \rangle$ part of Eq. (56). Since $\langle \Psi_1 | W | \Psi_3 \rangle = 0$ for the δ -function operator, the remainder comes from the $2\langle \Psi_0 | W | \Psi_4 \rangle$ part of Eq. (56).

There still remains the evaluation of nonadiabatic corrections. The calculation of these proceeds in exactly the same way as for the energy itself [11] to give $\Delta\beta_l$ and $\Delta\gamma$ terms in place of β_l and γ . Also, in parallel with the energy, the leading nonadiabatic correction to W_4 is [see Eq. (48) and the Appendix]

$$(\Delta W_4)_{\text{nonad}} = \frac{1}{2} (\beta_1 \Delta\alpha_1' + \alpha_1 \Delta\beta_1') (\langle x^{-8} \rangle - \langle x^{-4} \rangle^2) \quad (77)$$

and similarly

$$-W_0 (\Delta N_4)_{\text{nonad}} = \frac{1}{2} (\beta_1 \Delta\alpha_1'' + \alpha_1 \Delta\beta_1'') (\langle x^{-8} \rangle - \langle x^{-4} \rangle^2). \quad (78)$$

Collecting terms, the final result is

$$\begin{aligned} \langle W \rangle = & W_0 - \frac{1}{2} \Delta\alpha_1 \langle x^{-4} \rangle + \frac{1}{2} (-\Delta\alpha_2 + 6\Delta\beta_1) \langle x^{-6} \rangle + \frac{1}{2} (\Delta\delta + \frac{16}{5} \Delta\gamma) \langle x^{-7} \rangle \\ & + \frac{1}{2} \left[-\Delta\alpha_3 + 15\Delta\beta_2 - \Delta\epsilon + \beta_1 \Delta\alpha_1 + \alpha_1 \Delta\beta_1 - 72\Delta\gamma \left(1 + \frac{L(L+1)}{10} \right) \right] \langle x^{-8} \rangle \\ & + 2e_0^{(2)} \Delta\alpha_1 / \alpha_1 + \frac{1}{2} \alpha_1 \Delta\bar{\beta}_1' \langle x^{-4} \rangle^2 \end{aligned} \quad (79)$$

where

$$e_0^{(2)} = -\frac{1}{2} \alpha_1 \langle \chi_0^{(1)} | x^{-4} | \chi_0 \rangle. \quad (80)$$

A general expression for $e_0^{(2)}$ has been obtained by Drake and Swainson [15] and numerical values tabulated by Drachman [12]. General expressions for the expectation values $\langle x^{-k} \rangle$ are given by Bockasten [16] and extended by Drake and Swainson [17].

Unlike the energy formula, a term quadratic in $\langle x^{-4} \rangle$ still survives after the nonadiabatic corrections are added. The reason is that both energy denominators $D_m^2 D_n$ and $D_m D_n^2$ appear in the sixth term of Eq. (39) for $|\Psi_4\rangle$, while the nonadiabatic correction to W_4 gives only $D_m^2 D_n$ terms. Otherwise, Eq. (79) exactly parallels Eq. (49) for the energy if all linear replacements of α_l, β_l, \dots by $\Delta\alpha_l, \Delta\beta_l, \dots$ are made. An extra factor of 2 multiplies the $e_0^{(2)}$ term because the overall dependence of $e_0^{(2)}$ on α_1 is quadratic, and α_1^2 is replaced by $2\alpha_1 \Delta\alpha_1$.

Exact numerical values for the coefficients $\Delta\alpha_l, \Delta\beta_l, \dots$ can be systematically generated by repeated application of the method of Dalgarno and Lewis [18], as further discussed by Drachman [12] and Schwartz [19]. In brief, the equation

$$G_{k-1} |\varphi_0\rangle = [h_0(\mathbf{r}, Z), G_k] |\varphi_0\rangle, \quad (81)$$

starting with $G_0 = U^{(l)}$, can be solved analytically and

iterated as many times as necessary. The equation

$$\langle \varphi_m | U^{(l)} | \varphi_0 \rangle = (-D_m)^k \langle \varphi_m | G_k | \varphi_0 \rangle \quad (82)$$

is then used in the numerator of a perturbation expression to cancel a factor of D_m^k in the denominator. The summation over m is next completed by closure, and the process repeated until only a single expectation value is left.

The entire procedure above has been automated to evaluate an arbitrary expression of the types contained in Eqs. (58)–(68). The results are listed in Table I. Some of the results not involving powers of D_m in the denominators follow directly from the perturbation solutions $\varphi_0^{(j)}$ derived by Boyle *et al.* [20], provided that their solutions are renormalized so that $\langle \varphi_0^{(j)} | \varphi_0 \rangle = 0$.

D. Finite-nuclear-mass corrections

The results of the preceding section apply to the case of infinite nuclear mass. Finite-nuclear-mass effects are often taken into account by adding the mass-polarization operator $-(\mu/M)\nabla_r \cdot \nabla_x$ to the Hamiltonian. However, Drachman [14] has pointed out that a transformation to Jacobi coordinates enables the asymptotic expansions for the finite-mass corrections to be written down almost by inspection. The key point is that the multipole expansion (5) is replaced by

$$V = \frac{1}{x} \sum_{l=1}^{\infty} C_l \left[\frac{r}{x} \right]^l P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}}) \quad (83)$$

where

$$C_l = \frac{[(1-y)^l - Z(-1)^l y^l]}{(1-y^2)^{l+1}} \quad (84)$$

and $y = \mu/M$. The above extends Drachman's result to include the scaling with nuclear charge. Depending on the multipole contributions, each coefficient in the asymptotic potential is multiplied by combinations of C_l factors, leading to the replacements

$$\alpha_l \rightarrow C_l^2 \alpha_l, \quad \beta_l \rightarrow C_l^2 \beta_l, \\ \gamma \rightarrow C_1^2 \gamma, \quad \delta \rightarrow C_1^2 C_2 \delta,$$

$$\langle W \rangle_M = (1-3y) \langle W \rangle_{\infty} + y \left\{ -\Delta\alpha_1(Z-1) \langle x^{-4} \rangle + [2\Delta\alpha_2 + 6\Delta\beta_1(Z-1)] \langle x^{-6} \rangle + [\Delta\delta(Z-2) + \frac{16}{5}\Delta\gamma(Z-1)] \langle x^{-7} \rangle \right. \\ \left. + \left[3\Delta\alpha_3 - 30\Delta\beta_2 - 2\Delta\epsilon(Z-1) + 2\beta_1\Delta\alpha_1(Z-1) + 2\alpha_1\Delta\beta_1(Z-1) \right. \right. \\ \left. \left. - 72\Delta\gamma(Z-1) \left[1 + \frac{L(L+1)}{10} \right] \right] \langle x^{-8} \rangle + 8e_0^{(2)} \Delta\alpha_1(Z-1)/\alpha_1 \right. \\ \left. + 2\alpha_1 \Delta\tilde{\beta}'_1(Z-1) \langle x^{-4} \rangle^2 \right\}. \quad (85)$$

The first term is the reduced mass shift resulting from the a_{μ}^{-3} factor in Eq. (1), and the remainder is the specific mass shift, analogous to the corresponding normal and specific isotope shifts for the energy.

III. NUMERICAL RESULTS AND COMPARISON WITH VARIATIONAL CALCULATIONS

Recent developments in variational techniques with doubled basis sets and Hylleraas-type coordinates now allow high-precision calculations to be extended to the Rydberg states of helium [4-6]. In previous work [6], comparisons with asymptotic-expansion results have been presented for the energies and mass-polarization corrections. The purpose of this section is to make similar comparisons for the matrix elements of $\delta(\mathbf{r}_1)$. Preliminary values for some of the variational matrix elements have been published previously [6]. A full account of the variational calculations is in preparation.

Assuming (anti)symmetrized wave functions, the matrix element is

$$\pi \langle \Psi_0 | \delta(\mathbf{r}_1) | \Psi_0 \rangle = \frac{\pi}{2} \langle \Psi_0 | \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) | \Psi_0 \rangle \\ = \frac{Z^3}{2} \langle W \rangle a_{\mu}^{-3}, \quad (86)$$

with $\langle W \rangle$ given by Eq. (79). Following Drachman's [11] prescription for summing the asymptotic series, the terms included for $L \geq 4$ are

$$\langle W \rangle = 1 + W^{(4)} + W^{(6)} + \frac{1}{2}(W^{(7)} + W^{(8)}) + 2e_0^{(2)} \Delta\alpha_1/\alpha_1 \\ + \frac{1}{2}\alpha_1 \Delta\tilde{\beta}'_1 \langle x^{-4} \rangle^2 \pm \frac{1}{2}(W^{(7)} + W^{(8)}), \quad (87)$$

$$\epsilon \rightarrow C_1^4 \epsilon, \quad e_0^{(2)} \rightarrow C_1^4 e_0^{(2)},$$

and similarly for $\Delta\alpha_l, \Delta\beta_l, \dots$. Provided that μ/M is small, the C_l factors can be expanded according to

$$C_1^2 = 1 + 2(Z-1)y + [4 + (Z-1)^2]y^2 + \dots,$$

$$C_2^2 = 1 - 4y + (12 - 2Z)y^2 + \dots,$$

$$C_3^2 = 1 - 6y + 23y^2 + \dots,$$

$$C_4^2 = 1 + 4(Z-1)y + [8 + 6(Z-1)^2]y^2 + \dots,$$

$$C_1^2 C_2 = 1 + 2(Z-2)y + [7 - 5(Z-1) + (Z-1)^2]y^2 + \dots.$$

Keeping terms up to linear in y , the matrix element for finite mass is

where $W^{(k)}$ represents terms of order $\langle x^{-k} \rangle$ and the last term represents the uncertainty. For $L=3$, the terms are

$$\langle W \rangle = 1 + W^{(4)} + \frac{1}{2}W^{(6)} + 2e_0^{(2)} \Delta\alpha_1/\alpha_1 \\ + \frac{1}{2}\alpha_1 \Delta\tilde{\beta}'_1 \langle x^{-4} \rangle^2 \pm \frac{1}{2}W^{(6)}. \quad (88)$$

Since $Z^3/2=4$ for helium, the quantity $4\langle W \rangle - 4$ represents the correction to $\pi\langle\delta(\mathbf{r}_1)\rangle$ due to the presence of the outer electron. This is the quantity compared in Table II with the variational results obtained with the help of the Hiller *et al.* [2] global operator. The latter reduces the uncertainty by a factor of 20 or more. As an illustrative example, the individual contributions to $4\langle W \rangle$ for $n=10$ are listed in Table III. The $\langle x^{-4} \rangle^2$ term is negligible to this degree of accuracy. For helium, the leading terms are

$$\pi\langle\delta(\mathbf{r}_1)\rangle = 4 - \frac{31}{32} \langle x^{-4} \rangle + \frac{1447}{1024} \langle x^{-6} \rangle a_{\mu}^{-3}, \quad (89)$$

which is sufficiently accurate for many applications. The leading two terms agree with the preliminary result reported previously [6]. As an example from Table II, the complete matrix element for the $10L$ state is

$$\langle\delta(\mathbf{r})\rangle_{10L} = 3.999\,999\,974\,685\,9(1)a_{\mu}^{-3}.$$

However, for many applications such as the calculation of ionization energies and energy differences, $\langle\delta(\mathbf{r})\rangle - 4$ is the quantity of direct physical interest.

The results in Table II show the very rapid improvement of the asymptotic-expansion (AE) values with increasing L . For $L=3$ and 4, the AE values are less accurate than the variational results, but the differences are in

TABLE II. Comparison of values for $\pi\langle\delta(\mathbf{r})\rangle - 4$ (units of 10^{-6} a.u.).

L	n	Variational calculation		Asymptotic expansion	Difference ^a
		Singlet	Triplet		
3	4	-35.183 0(1) ^b	-35.397 3(1)	-35.6(6)	0.3(6)
3	5	-20.052 7(3)	-20.232 5(4)	-20.3(4)	0.2(4)
3	6	-12.244 7(1)	-12.373 2(2)	-12.42(27)	0.11(27)
3	7	-7.953 6(2)	-8.044 6(3)	-8.07(19)	0.07(19)
3	8	-5.433 73(4)	-5.499 2(1)	-5.52(13)	0.05(13)
3	9	-3.867 2(1)	-3.915 33(2)	-3.93(10)	0.04(10)
3	10	-2.845 3(4)	-2.881 82(2)	-2.89(7)	0.03(7)
4	5	-4.886 44(2)	-4.886 78(1)	-4.886 6(22)	0.000 0(22)
4	6	-3.135 6(1)	-3.135 9(1)	-3.136 0(25)	0.000 2(25)
4	7	-2.091 7(3)	-2.091 7(3)	-2.091 8(22)	0.000 1(22)
4	8	-1.452 0(1)	-1.452 3(1)	-1.452 2(18)	0.000 1(18)
4	9	-1.044 27(1)	-1.044 47(1)	-1.044 4(14)	0.000 0(14)
4	10	-0.774 00(1)	-0.774 12(2)	-0.774 1(11)	0.000 0(11)
5	6	-1.003 9(2)	-1.004 0(2)	-1.003 93(1)	-0.000 0(2)
5	7	-0.696 15(2)	-0.696 16(2)	-0.696 13(2)	-0.000 02(2)
5	8	-0.494 16(1)	-0.494 15(1)	-0.494 14(3)	-0.000 02(3)
5	9	-0.360 3(2)	-0.360 3(2)	-0.360 43(3)	0.000 10(20)
5	10	-0.269 71(7)	-0.269 65(6)	-0.269 72(2)	0.000 04(9)
6	7	-0.268 36(1)	-0.268 37(1)	-0.268 369(3)	0.000 004(14)
6	8	-0.196 56(1)	-0.196 56(2)	-0.196 564(1)	0.000 004(22)
6	9	-0.146 11(4)	-0.146 11(3)	-0.146 131(1)	0.000 021(50)
6	10	-0.110 74(1)	-0.110 75(1)	-0.110 741(1)	-0.000 004(15)
7	8	-0.086 575(3)	-0.086 575(3)	-0.086 575 2(5)	0.000 000 2(42)
7	9	-0.066 047 8(3)	-0.066 048 3(6)	-0.066 046 0(4)	-0.000 002 0(8)
7	10	-0.050 881(3)	-0.050 881(3)	-0.050 880 4(3)	-0.000 000 6(42)
8	9			-0.032 155 8(1)	
8	10			-0.025 314 1(1)	

^aDifference between the singlet-triplet average and the asymptotic value.

^bNumbers in parentheses denote the uncertainties in the final one or two figures quoted.

good accord with the uncertainty estimates from Eqs. (87) and (88). In fact, for $L=4$, the AE values are fortuitously much better than what the uncertainty estimate would indicate, although of course the AE values do not contain the singlet-triplet splittings. Something similar was found previously for the $L=4$ energies [6]. For $L \geq 5$, the singlet-triplet splittings become negligible, and the AE values exceed the variational results in accuracy. In this region, the comparison should be interpreted as a test of the variational results rather than the AE values. In particular, the comparison confirms the uncertainty

estimates for the variational matrix elements as derived from the apparent convergence with the size of the basis set. Only for the case $L=7$, $n=9$ is the apparent accuracy overestimated.

Table IV presents a similar comparison for the specific-mass corrections to $\pi\langle\delta(\mathbf{r}_1)\rangle$. The AE values are obtained from the terms in braces in Eq. (85). For helium, the leading terms in this case are

$$\pi\Delta\langle\delta(\mathbf{r}_1)\rangle_M = (\mu/M)\left(-\frac{31}{16}\langle x^{-4}\rangle + \frac{4789}{512}\langle x^{-6}\rangle\right) \quad (90)$$

TABLE III. Individual contributions to $\pi\langle\delta(\mathbf{r})\rangle$ for $n=10$ (in units of 10^{-6} a.u.).

Contribution	L	3	4	5	6	7	8
$4\mathcal{W}^{(4)}$		-2.952	-0.7828	-0.270 98	-0.110 972 4	-0.050 931 9	-0.025 326 80
$4\mathcal{W}^{(6)}$		0.144	0.0102	0.001 32	0.000 237 4	0.000 052 2	0.000 012 86
$4\mathcal{W}^{(7)}$			0.0027	0.000 20	0.000 022 9	0.000 003 4	0.000 000 59
$4\mathcal{W}^{(8)}$			-0.0049	-0.000 25	-0.000 022 8	-0.000 002 9	-0.000 000 43
$8e_0^{(2)}\Delta\alpha_1/\alpha_1$		-0.009	-0.0004	-0.000 04	-0.000 005 5	-0.000 001 0	-0.000 000 20
Total		-2.890	-0.7741	-0.269 72	-0.110 740 5	-0.050 880 4	-0.025 314 07
Uncertainty		0.072	0.0011	0.000 02	0.000 000 0	0.000 000 3	0.000 000 08

with $\mu/M = 1.370\,745\,620 \times 10^{-3}$ for ${}^4\text{He}$. The variational results are less accurate by approximately this factor of μ/M because they were obtained by taking the small difference between the matrix elements both with and without the mass-polarization term included in the Hamiltonian. As a result, they match or exceed the accuracy of the AE values only for $L \leq 3$. In this range, there is also a significant singlet-triplet splitting which is not contained in the AE calculation. However, for $L \geq 4$, the singlet-triplet splitting becomes negligible and the AE values become much more accurate than the variational results. In this range, the comparison in Table IV provides an important test of the apparent convergence of the variational calculations. The variational results include an additional mass-dependent correction to the global operator [5].

IV. DISCUSSION

Variational methods are particularly successful in obtaining accurate values for the energy because this is the quantity which is optimized. By construction, the variational eigenvalues are stable with respect to first-order variations in the wave function. In general, this is not the

case for other matrix elements and, as a rough rule of thumb, N significant figures for the energy correspond to $N/2$ significant figures for other atomic properties. The results of this paper show the remarkable utility of asymptotic-expansion methods for calculating atomic properties of Rydberg states other than the energy. Unlike the variational method, the accuracy is about the same as for the energy itself, and the calculations are easily extended to arbitrarily high nL states. The analysis leading up to Eq. (79) takes advantage of a number of simplifications which occur for the special case of δ -function matrix elements. However, no new problems occur when the terms that were dropped following Eq. (74) are retained and the method applied to the calculation of matrix elements of other operators (provided that the operator is not too singular [12]). There is considerable scope for future developments along these lines.

The particular significance of the results obtained for matrix elements of the δ function is that for $L \geq 5$ (see Table II) it reduces the dominant source of uncertainty in the Breit interaction correction to the energies of the Rydberg states of helium, obtained by the variational method [4–6,9]. A full discussion of the variational results is planned to be presented in a forthcoming publication.

TABLE IV. Comparison of values for the specific-mass correction to $\pi\langle\delta(\mathbf{r})\rangle$ (units of $10^{-6} \mu/M$ a.u.).

L	n	Variational calculation		Asymptotic expansion	Difference ^a
		Singlet	Triplet		
3	4	-67(2)	-64(2)	-68.8(3.6)	3.3(4.6)
3	5	-39(1)	-36(1)	-38.9(2.7)	1.4(3.0)
3	6	-23(1)	-21(2)	-23.7(1.8)	1.7(2.9)
3	7	-16(1)	-13(1)	-15.3(1.2)	0.8(1.9)
3	8	-10(1)	-8(2)	-10.5(9)	1.5(24)
3	9	-7.0(4)	-6.5(2)	-7.4(6)	0.7(7)
3	10	-5.1(4)	-4.3(4)	-5.5(5)	0.8(8)
4	5	-9.3(6)	-9.2(6)	-9.61(1)	0.4(8)
4	6	-6.0(7)	-6.1(2)	-6.13(1)	0.1(7)
4	7	-3.9(2)	-3.6(2)	-4.08(1)	0.3(3)
4	8	-3.2(4)	-3.5(7)	-2.828(8)	0.5(8)
4	9	-2.7(1.0)	-2.2(5)	-2.031(6)	-0.4(1.1)
4	10	-1.6(4)	-1.5(4)	-1.505(5)	-0.5(6)
5	6	-2.0(3)	-2.1(2)	-1.994 9(3)	-0.05(36)
5	7	-1.4(1)	-1.4(1)	-1.380 5(4)	-0.02(14)
5	8	-0.9(4)	-1.0(4)	-0.978 8(3)	0.03(56)
5	9	-0.6(4)	-0.5(4)	-0.713 4(3)	0.16(56)
5	10	-0.57(5)	-0.59(2)	-0.533 6(2)	-0.05(6)
6	7	-0.56(7)	-0.55(5)	-0.535 14(2)	-0.02(8)
6	8	-0.35(2)	-0.31(5)	-0.391 61(2)	0.06(5)
6	9	-0.27(1)	-0.27(1)	-0.290 97(2)	0.02(2)
6	10	-0.16(5)	-0.17(5)	-0.220 42(2)	0.05(8)
7	8	-0.17(1)	-0.18(2)	-0.172 879(2)	0.003(22)
7	9	-0.131(2)	-0.126(6)	-0.131 825(2)	-0.004(6)
7	10	-0.103(3)	-0.103(2)	-0.101 525(2)	-0.002(4)
8	9			-0.064 253 6(2)	
8	10			-0.050 569 7(3)	

^aDifference between the singlet-triplet average and the asymptotic value.

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APPENDIX: EVALUATION OF NONADIABATIC CORRECTIONS

The purpose of this appendix is to discuss the nonadiabatic corrections which occur in the terms E_4 , W_4 , and $-W_0N_4$. Although no explicit use of the optical potential is made, parts of the derivations resemble those given previously by Drachman [11].

The $e_0^{(2)}$ term in E_4 provides a simple example to illustrate the techniques required. It comes from the evaluation of

$$e_0^{(2)} = \langle \Psi_1 | V | \varphi_0 \chi_0^{(1)} \rangle, \quad (\text{A1})$$

where $|\Psi_1\rangle$ and $|\varphi_0 \chi_0^{(1)}\rangle$ are given by Eqs. (34) and (36a), respectively. Each contains a factor of $1/D_m$, which generates nonadiabatic corrections upon the replacement

$$|\varphi_0 \chi_0^{(1)}\rangle_{\text{nonad}} = \frac{1}{2} \beta_1 |\varphi_0\rangle \sum_{n,\mu} \frac{1}{d_n} ([u^{(1,\mu)*}, \hat{h}] u^{(1,\mu)} + u^{(1,\mu)*} [\hat{h}, u^{(1,\mu)}] + u^{(1,\mu)*} u^{(1,\mu)} \hat{h})_{0,n} |\chi_n\rangle. \quad (\text{A6})$$

Using the fact that $\nabla^2 u^{(1,\mu)} = 0$, the commutators reduce to

$$[\hat{h}, u^{(1,\mu)}] = -\nabla u^{(1,\mu)} \cdot \nabla$$

and so the $(0, n)$ matrix element becomes

$$\begin{aligned} & ([u^{(1,\mu)*}, \hat{h}] u^{(1,\mu)} + u^{(1,\mu)*} [\hat{h}, u^{(1,\mu)}])_{0,n} \\ &= - \int d\mathbf{x} [(\nabla \chi_0^*) \cdot (\nabla u^{(1,\mu)*}) u^{(1,\mu)} \chi_0 \\ & \quad + \chi_0^* u^{(1,\mu)*} (\nabla u^{(1,\mu)}) \cdot (\nabla \chi_0)]. \quad (\text{A7}) \end{aligned}$$

Since $(\nabla u^{(1,\mu)*}) u^{(1,\mu)} = (\nabla u^{(1,-\mu)}) u^{(1,-\mu)*}$, the $+\mu$ and $-\mu$ contributions can be combined to give

$$\begin{aligned} & \sum_{n,\mu} ([u^{(1,\mu)*}, \hat{h}] u^{(1,\mu)} + u^{(1,\mu)*} [\hat{h}, u^{(1,\mu)}])_{0,n} \\ &= -\frac{1}{2} \sum_{n,\mu} \int d\mathbf{x} \nabla(\chi_0^* \chi_n) \cdot \nabla |u^{(1,\mu)}|^2 \\ &= \frac{1}{2} \sum_{n,\mu} \int d\mathbf{x} \chi_0^* \chi_n \nabla^2 |u^{(1,\mu)}|^2, \quad (\text{A8}) \end{aligned}$$

where an integration by parts has been done. Using Eq. (30), $\sum_{\mu} |u^{(1,\mu)}|^2 = 1/x^4$ and $\nabla^2(1/x^4) = 12/x^6$. Substituting (A8) into (A6) yields

$$|\varphi_0 \chi_0^{(1)}\rangle_{\text{nonad}} = \frac{1}{2} \beta_1 |\varphi_0\rangle \sum_n \frac{1}{d_n} (6x^{-6} + x^{-4} \hat{h})_{0,n} |\chi_n\rangle. \quad (\text{A9})$$

Defining $\chi_0^{(1)}(j)$ to be the solution to the perturbation equation

$$1/D_m \rightarrow 1/D_m - d_{m'}/D_m^2 + \dots \quad (\text{A2})$$

For the case of $e_0^{(2)}$, these turn out to be equal so that it is only necessary to evaluate

$$|\varphi_0 \chi_0^{(1)}\rangle_{\text{nonad}} = \sum_{m,n_0} \frac{V_{0,m}(-d_{m'}) V_{m,n_0} |n_0\rangle}{D_m^2 d_n} \quad (\text{A3})$$

and multiply by 2. Replacing $-d_{m'}$ by the operator

$$\hat{h} = h_0(\mathbf{x}, Z-1) - e_0 \quad (\text{A4})$$

acting on $\chi_{m'}$ and expanding the matrix elements into one-electron dipole factors results in

$$\begin{aligned} |\varphi_0 \chi_0^{(1)}\rangle_{\text{nonad}} &= |\varphi_0\rangle \sum_{m,\mu} (-1)^\mu \frac{U_{0,m}^{(1,\mu)} U_{m,0}^{(1,-\mu)}}{D_m^2} \\ & \quad \times \sum_{m',n} \frac{u_{0,m'}^{(1,\mu)} \hat{h} u_{m',n}^{(1,\mu')}}{d_n} |\chi_n\rangle. \quad (\text{A5}) \end{aligned}$$

The first summation is just the definition of β_1 . In the second summation, commute \hat{h} to the left and to the right, take the average, and complete the sum over m' by closure to obtain

$$\hat{h} \chi_0^{(1)}(j) = (\langle x^{-j} \rangle - x^{-j}) \chi_0, \quad (\text{A10})$$

then the first term of (A9) is proportional to $\chi_0^{(1)}(6)$ and the second term (without the \hat{h}) is proportional to $\chi_0^{(1)}(4)$. Thus $\hat{h} \chi_0^{(1)}(4)$ can be replaced by the right-hand side of (A10) with $j=4$. The final result is

$$|\varphi_0 \chi_0^{(1)}\rangle_{\text{nonad}} = \frac{1}{2} \beta_1 |\varphi_0\rangle [6\chi_0^{(1)}(6) + (\langle x^{-4} \rangle - x^{-4}) \chi_0]. \quad (\text{A11})$$

The $\chi_0^{(1)}(6)$ part of (A11) can be neglected. The remainder gives the nonadiabatic correction to E_4 (with an extra factor of 2 included as discussed above)

$$(\Delta E_4)_{\text{nonad}} = \frac{1}{2} \alpha_1 \beta_1 (\langle x^{-8} \rangle - \langle x^{-4} \rangle^2)$$

in agreement with Eq. (48).

A closely parallel analysis applies to the δ -function matrix elements. The terms $-\Delta\alpha'_1 \langle \chi_0^{(1)} | x^{-4} | \chi_0 \rangle$ in W_4 [Eq. (76)] and $-\Delta\alpha'_1 \langle \chi_0^{(1)} | x^{-4} | \chi_0 \rangle$ in $-W_0N_4$ [Eq. (71)] come from the evaluation of the quantities

$$T' = 4 \sum_{m,n} \frac{\langle \varphi_0 \chi_0^{(1)} | V | m \rangle V_{m,n} W_{n,0}}{D_m D_n} \quad (\text{A12})$$

and

$$T'' = -2 W_0 \sum_m \frac{\langle \varphi_0 \chi_0^{(1)} | V | m \rangle V_{m,0}}{D_m^2}. \quad (\text{A13})$$

The nonadiabatic corrections consists of two parts. The first part comes from the replacement $|\varphi_0 \chi_0^{(1)}\rangle$

→ $|\varphi_0\chi_0^{(1)}\rangle_{\text{nonad}}$ to give

$$(\Delta T'_1)_{\text{nonad}} = \frac{1}{2}\beta_1\Delta\alpha'_1(\langle x^{-8}\rangle - \langle x^{-4}\rangle^2), \quad (\text{A14})$$

$$(\Delta T''_1)_{\text{nonad}} = \frac{1}{2}\beta_1\Delta\alpha''_1(\langle x^{-8}\rangle - \langle x^{-4}\rangle^2). \quad (\text{A15})$$

The second part comes from the nonadiabatic corrections to the denominators in (A12) and (A13). There is no contribution from D_n in (A12) because W only affects the inner electron and hence, by orthonality, $W_{n,0} = 0$ unless $|n\rangle = |\varphi_n\chi_0\rangle$. What remains is

$$(\Delta T'_2)_{\text{nonad}} = 4 \sum_{m,n} \frac{\langle \varphi_0\chi_0^{(1)} | V | m \rangle \hat{h} V_{m,n} W_{n,0}}{D_m^2 D_n}, \quad (\text{A16})$$

and

$$(\Delta T''_2)_{\text{nonad}} = -4W_0 \sum_m \frac{\langle \varphi_0\chi_0^{(1)} | V | m \rangle \hat{h} V_{m,0}}{D_m^3}. \quad (\text{A17})$$

Commuting \hat{h} to the left and right as above and again using Eq. (A10), the above reduce to

$$(\Delta T'_2)_{\text{nonad}} = \frac{1}{2}\alpha_1\Delta\beta'_1(\langle x^{-8}\rangle - \langle x^{-4}\rangle^2), \quad (\text{A18})$$

$$(\Delta T''_2)_{\text{nonad}} = \frac{1}{2}\alpha_1\Delta\beta''_1(\langle x^{-8}\rangle - \langle x^{-4}\rangle^2). \quad (\text{A19})$$

Adding the contributions (A14) plus (A18) and (A15) plus (A19) gives Eqs. (77) and (78), respectively.

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