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Energies for the high- L Rydberg states of helium: Asymptotic analysis

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The asymptotic expansion method based on a core polarization potential for the Rydberg electron is reviewed and extended to the high angular momentum states of helium up to $L=15$. A comparison with recent large-scale configuration interaction calculations for the nonrelativistic energies shows that there is good agreement for $L=7$, but there are serious systematic disagreements for the states of higher angular momentum. A possible explanation is that there is an important class of configurations missing from the CI calculations.

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I. INTRODUCTION

The helium atom is the simplest atomic system that cannot be solved exactly, even in the nonrelativistic limit with purely Coulombic interactions. Despite recent advances for the low-lying states [2–4], it continues to provide important computational challenges for the higher-lying Rydberg states. Traditional variational methods, such as those used in the early work of Pekeris and co-workers [5], tend to deteriorate rapidly in accuracy as one goes up the Rydberg series of states of a given symmetry. At the same time, the accuracy requirements for transition frequencies between Rydberg states with the same principal quantum number n become more stringent since these differences go to zero as $1/n^3$ with increasing n . For example, for the $1s10i\ ^1I$ and $1s10k\ ^1K$ states of helium ($L=6$ and 7 , respectively), the nonrelativistic energies are

$$E_{\infty}(1s10i\ ^1I) = -2.005\ 000\ 016\ 086\ 516\ 194(2)\ \text{a.u.},$$

$$E_{\infty}(1s10k\ ^1K) = -2.005\ 000\ 007\ 388\ 375\ 877(1)\ \text{a.u.}$$

and so 10 figure accuracy is needed in the total energy just to get the first figure correct in the $10I-10K$ transition energy. The first several figures are simply given by the screened hydrogenic energy $E_{SH} = -2 - 1/2n^2$ that can be trivially calculated. Thus, absolute accuracies that are perfectly adequate for the low-lying states may be of no use for transitions among the Rydberg states. Such transitions continue to be of interest in connection with measurements of the polarizability of the ion core, and the Casimir-Polder effect [6,7].

Our previous comprehensive survey of the Rydberg states of helium covered all states up to $n=10$ and $L=7$ [8–10], and their extension to higher n via quantum defect theory [11]. These variational calculations employed a double basis set in Hylleraas coordinates involving two sets of distance scales that were individually optimized. The basis sets also included explicitly the screened hydrogenic term. With these modifications, high accuracy was achieved for the Rydberg states, at least up to $n=10$, with reasonably small basis sets. A key conclusion of this work was that there is no point in doing variational calculations for $L > 7$ because alternative calculations based on the asymptotic expansion method provide a more than sufficient level accuracy that is very difficult to exceed by direct variational calculations.

The purpose of the present Brief Report is to review and extend the results of the asymptotic expansion method, and to compare with the results of recent large-scale configuration interaction (CI) calculations for the Rydberg states of helium [1]. It will be seen that there are serious disagreements with the results of the CI calculations.

II. ASYMPTOTIC EXPANSION METHOD

The asymptotic expansion method was originally developed by Drachman [12,13] from an expansion of the optical potential for the Rydberg electron in powers of the perturbing potential, and later reformulated by Drake [9,10] based on a simple perturbation expansion for the total wave function. The method takes advantage of the fact that, with increasing angular momentum, the overlap of the Rydberg electron wave function with the core consisting of a $1s$ electron and the nucleus becomes vanishingly small. As shown in Table I, the singlet-triplet splittings for $n=10$ go to zero exponentially fast in proportion to $\exp(-6.3L)$. Exchange and short-range effects can then be neglected for sufficiently large L and the Rydberg electron treated as a distinguishable

TABLE I. Variational energies and singlet-triplet (S-T) splittings for the $n=10$ states of helium. Units are atomic units.

State	Energy	S-T splitting ($\times 10^3$)
$10\ ^1S$	-2.005 142 991 747 992 6(1) ^a	
$10\ ^3S$	-2.005 310 794 915 611 3(1)	0.167 803 167 618 7
$10\ ^1P$	-2.004 987 983 802 217 9(26)	
$10\ ^3P$	-2.005 068 805 497 706 7(30)	0.080 821 695 488 8
$10\ ^1D$	-2.005 002 071 654 256 81(75)	
$10\ ^3D$	-2.005 002 818 080 228 84(53)	0.000 746 425 972 0
$10\ ^1F$	-2.005 000 417 564 668 80(11)	
$10\ ^3F$	-2.005 000 421 686 604 88(26)	0.000 004 121 936 08 ^a
$10\ ^1G$	-2.005 000 112 764 318 746(22)	
$10\ ^3G$	-2.005 000 112 777 003 317(21)	0.000 000 012 684 571
$10\ ^1H$	-2.005 000 039 214 394 532(17)	
$10\ ^3H$	-2.005 000 039 214 417 416(17)	0.000 000 000 022 884
$10\ ^1I$	-2.005 000 016 086 516 194 7(3)	
$10\ ^3I$	-2.005 000 016 086 516 219 4(3)	0.000 000 000 000 025
$10\ ^1K$	-2.005 000 007 388 375 876 9(0)	
$10\ ^3K$	-2.005 000 007 388 375 876 9(0)	0.000 000 000 000 000

^aReference [4].

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particle moving in the effective field generated by the core. The core itself distorts in response to the electric field of the Rydberg electron, as characterized by the multipole moments of the core. The result is an asymptotic potential in powers of $1/x$ as in Eq. (1), where x is the radial coordinate of the Rydberg electron. The method can also be applied to the calculation of quantities other than the energy, such as matrix elements of the δ function [14].

For a heliumlike atomic system, the multipole moments of the one-electron core can be calculated exactly. The result is an effective potential for the Rydberg electron expressed as an asymptotic expansion of the form

$$V(x) = -\frac{Z-1}{x} - \frac{1}{2} \sum_{j=4}^p c_j x^{-j}, \quad (1)$$

where $Z-1$ is the screened nuclear charge, and the c_j are related to the multipole moments of the core. Since expectation values $\langle 1/x^j \rangle_{nL}$ with respect to the Rydberg electron diverge for $j > 2L+2$, the summation in Eq. (1) must be truncated at a judiciously chosen value of $p \leq 2L+2$ where the terms begin increasing in size. For this reason, L must be sufficiently large that enough terms can be included for good convergence. For helium, the asymptotic expansion becomes essentially exact relative to experimental accuracy and variational calculations for $L > 7$. Beyond this point, the asymptotic expansion provides a simple analytic method for calculating energies that applies to all high- nL Rydberg states.

The starting point is to write the total Hamiltonian for helium in the form

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

where

$$H_0(r, x) = -\frac{1}{2} \nabla_r^2 - \frac{Z}{r} - \frac{1}{2} \nabla_x^2 - \frac{Z-1}{x} \quad (3)$$

is the screened hydrogenic Hamiltonian for infinite nuclear mass, and

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

is the correction to the screened hydrogenic potential. Here, \mathbf{r} denotes the position vector of the inner electron and \mathbf{x} the position vector of the Rydberg electron. The correction potential has the multipole expansion

$$V(\mathbf{r}, \mathbf{x}) = \frac{1}{x} \sum_{\ell=1}^{\infty} \left(\frac{r}{x} \right)^{\ell} P_{\ell}(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}}) \quad (5)$$

in the asymptotic region with $x > r$, where the $P_{\ell}(\cos \theta)$ are Legendre polynomials.

We now expand the solution to the full Schrödinger equation

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

as a perturbation series with V as the perturbation according to $\Psi(r, x) = \sum_{j=0}^{\infty} \Psi_j(r, x)$ and $E = \sum_{j=0}^{\infty} E_j$ where

$$(H_0 - E_0) \Psi_0(r, x) = 0 \quad (7)$$

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

$$(H_0 - E_0) \Psi_j + V \Psi_{j-1} = \sum_{k=1}^j E_k \Psi_{j-k}. \quad (8)$$

It follows from Eq. (8) that

$$E_j = \langle \Psi_0 | V | \Psi_{j-1} \rangle \quad (9)$$

E_1 goes to zero exponentially with L and as shown by Drachman [12], can be neglected for states with $L > 4$. Energies beyond E_4 only contribute terms of order x^{-11} and smaller, and they are therefore not needed for the present calculation. All the perturbed wave functions are defined in Ref. [10], leading to the asymptotic expansion

$$E_{nL} = -2 - \frac{1}{2n^2} - \sum_{i=4}^p \frac{c_i}{2} \langle x^{-i} \rangle_{nL} + e_2^{(1,1)} - \frac{23}{20} e_2^{(1,2)} + \dots \quad (10)$$

for helium ($Z=2$). The c_i are coefficients related to the multipole polarizabilities and other properties characterizing the response of the core to the perturbing field of the Rydberg electron. For example $c_4 = \alpha_1 = \frac{9}{32} a_0^3$, $c_5 = 0$, and $c_6 = \alpha_2 - 6\beta_1$, where α_i is the 2^i -pole polarizability, and β_1 is a nonadiabatic correction to α_1 . The numerical values for helium are $\alpha_2 = \frac{19}{64} a_0^5$ and $\beta_1 = \frac{43}{512} a_0^5$. The c_i are known in their entirety up to c_{10} , as tabulated by [10]. The hydrogenic expectation values $\langle x^{-i} \rangle_{nL}$ for the Rydberg electron can easily be calculated analytically [15,16]. The quantities $e_2^{(1,1)}$ and $e_2^{(1,2)}$ are second-order corrections due to the dipole and quadrupole adiabatic terms in the asymptotic potential, as explained in detail by Swainson and Drake [17].

After substituting the exact analytic values for the various multipole polarizabilities [10], the asymptotic expansion (10) for the energy levels of helium becomes

$$\begin{aligned} E_{nL} = & -2 - \frac{1}{2n^2} - \frac{1}{2} \left\{ -\frac{9}{32} \langle x^{-4} \rangle + \frac{69}{256} \langle x^{-6} \rangle + \frac{3833}{7680} \langle x^{-7} \rangle \right. \\ & - \left[\frac{55\,923}{32\,768} + \frac{957}{5120} L(L+1) \right] \langle x^{-8} \rangle - \frac{908\,185}{344\,064} \langle x^{-9} \rangle \\ & \left. + \left[\frac{3\,824\,925}{524\,288} + \frac{33\,275}{14\,336} L(L+1) \right] \langle x^{-10} \rangle \right\} \\ & + e_2^{(1,1)} - \frac{23}{20} e_2^{(1,2)} \end{aligned} \quad (11)$$

III. RESULTS AND DISCUSSION

As an example, Table II shows the contributions to the energy of the $n=15$, $L=10$ state of helium. The uncertainty is taken to be one half of the c_{10} term.

Table III compares the results of the asymptotic expansion (AE) with the large-scale CI calculations of Kamta *et al.* [1]. To make the physically important polarization corrections stand out more clearly, the screened hydrogenic energy

TABLE II. Breakdown of contributions to the nonrelativistic energy for the $n=15$, $L=10$ state of helium.

Quantity	Value (a.u)
$-\frac{1}{2}Z^2$	-2.000 000 000 000 000 000 0
$-\frac{1}{2n^2}$	-0.002 222 222 222 222 222 2
$\frac{1}{2}c_4\langle x^{-4} \rangle$	-0.000 000 000 414 592 329 2
$\frac{1}{2}c_6\langle x^{-6} \rangle$	0.000 000 000 000 072 901 7
$\frac{1}{2}c_7\langle x^{-7} \rangle$	0.000 000 000 000 002 008 3
$\frac{1}{2}c_8\langle x^{-8} \rangle$	-0.000 000 000 000 001 402 1
$\frac{1}{2}c_9\langle x^{-9} \rangle$	-0.000 000 000 000 000 002 7
$\frac{1}{2}c_{10}\langle x^{-10} \rangle$	0.000 000 000 000 000 004 7
Second order	-0.000 000 000 000 000 529 0
Total	-2.002 222 222 636 741 570 4
Uncertainty	$\pm 0.000 000 000 000 000 002 4$

$-2-1/2n^2$ is subtracted from both, and the difference displayed. For $L=7$, most of the differences are within one or two standard deviations of the estimated accuracy of the

asymptotic expansions. The one exception is the $n=12$ state, where the CI value is substantially lower than the AE value. However, for $L=10$ and $L=11$, the differences are very much larger by a factor of nearly 10^6 , such that the CI results do not reproduce the leading $c_4\langle x^{-4} \rangle$ dipole polarization correction. Using the formula

$$\langle x^{-4} \rangle = \frac{16[3n^2 - L(L+1)]}{n^5(2L+3)(2L+2)(2L+1)(2L)(2L-1)} \quad (12)$$

and $c_4 = \alpha_1 = 9/32$, a simple hand calculation with $n=15$ and $L=10$ yields the correction $c_4\langle x^{-4} \rangle/2 = -4.145923 \times 10^{-10}$ a.u. as shown in Table II. This is more than twice as big in magnitude as the CI value -1.976×10^{-10} a.u. from Table III.

Table IV summarizes the asymptotic expansion results for the nonrelativistic energies and their estimated uncertainties for all the remaining states up to and including $L=15$. It would be a significant challenge indeed to match this level of accuracy with direct CI or Hylleraas-type variational calculations.

The corresponding asymptotic expansions are known for the finite nuclear mass (mass polarization) corrections,

TABLE III. Comparison of the asymptotic expansion (AE) energies with the CI results of Kamta *et al.* [1] for $L=7$ (K-states), $L=10$, and $L=11$ of helium. Units are atomic units.

L	n	E_{AE}	$E_{AE}+2+1/2n^2$	$E_{CI}+2+1/2n^2$	Difference $\times 10^{15}$
7	8	-2.007 812 512 570 229 3(11)	-0.000 000 012 570 229 3(11)	-0.000 000 012 570 227	2.3(1.1)
	9	-2.006 172 849 096 329 8(17)	-0.000 000 009 590 156 9(17)	-0.000 000 009 590 156	0.8(1.7)
	10	-2.005 000 007 388 375 8(19)	-0.000 000 007 388 375 8(19)	-0.000 000 007 388 375	0.8(1.9)
	11	-2.004 132 237 176 715 3(18)	-0.000 000 005 771 756 7(18)	-0.000 000 005 771 758	-1.7(1.8)
	12	-2.003 472 226 797 270 3(17)	-0.000 000 004 575 048 1(17)	-0.000 000 004 575 059	-11.0(1.7)
	13	-2.002 958 583 559 214 5(15)	-0.000 000 003 677 557 7(15)	-0.000 000 003 677 554	3.5(1.5)
	14	-2.002 551 023 402 909 7(13)	-0.000 000 002 994 746 4(13)	-0.000 000 002 994 744	2.7(1.3)
10	15	-2.002 222 224 690 046 0(12)	-0.000 000 002 467 823 8(12)	-0.000 000 002 467 821	3.0(1.2)
	16	-2.001 953 127 055 667 0(10)	-0.000 000 002 055 667 0(10)	-0.000 000 002 055 667	0.0(1.0)
	17	-2.001 730 105 535 420 0(09)	-0.000 000 001 729 191 6(09)	-0.000 000 001 729 190	2.0(0.9)
	11	-2.004 132 232 280 227 020 2(11)	-0.000 000 000 875 268 342 6(11)	-0.000 000 000 417 089	458 179.
	12	-2.003 472 222 943 200 228 6(18)	-0.000 000 000 720 978 006 3(18)	-0.000 000 000 343 625	377 353.
	13	-2.002 958 580 477 370 602 9(22)	-0.000 000 000 595 713 798 1(22)	-0.000 000 000 283 955	311 759.
	14	-2.002 551 020 903 322 957 3(24)	-0.000 000 000 495 159 692 0(24)	-0.000 000 000 236 054	259 106.
	15	-2.002 222 222 636 741 570 4(24)	-0.000 000 000 414 519 348 2(24)	-0.000 000 000 197 624	216 896.
	16	-2.001 953 125 349 602 670 8(23)	-0.000 000 000 349 602 670 8(23)	-0.000 000 000 166 681	182 921.
	17	-2.001 730 104 103 256 030 2(22)	-0.000 000 000 297 027 656 5(22)	-0.000 000 000 141 623	155 405.
11	18	-2.001 543 210 130 691 840 5(20)	-0.000 000 000 254 148 630 6(20)	-0.000 000 000 121 186	132 963.
	19	-2.001 385 041 770 166 678 6(18)	-0.000 000 000 218 920 141 3(18)	-0.000 000 000 104 390	114 530.
	20	-2.001 250 000 189 764 772 4(17)	-0.000 000 000 189 764 772 4(17)	-0.000 000 000 090 496	99 269.
	12	-2.003 472 222 647 669 786 6(2)	-0.000 000 000 425 447 564 4(1.8)	-0.000 000 000 203 585	221 863.
	13	-2.002 958 580 238 056 972 3(3)	-0.000 000 000 356 400 167 6(3.0)	-0.000 000 000 170 565	185 835.
	14	-2.002 551 020 707 350 071 8(4)	-0.000 000 000 299 186 806 5(3.7)	-0.000 000 000 143 197	155 990.
	15	-2.002 222 222 474 545 323 5(4)	-0.000 000 000 252 323 101 3(4.1)	-0.000 000 000 120 776	131 547.
	16	-2.001 953 125 214 026 381 7(4)	-0.000 000 000 214 026 381 7(4.2)	-0.000 000 000 102 446	111 580.
	17	-2.001 730 103 988 891 183 1(4)	-0.000 000 000 182 662 809 4(4.1)	-0.000 000 000 087 441	95 222.
	18	-2.001 543 210 033 406 727 9(4)	-0.000 000 000 156 863 518 0(3.9)	-0.000 000 000 075 090	81 774.
	19	-2.001 385 041 686 770 431 0(4)	-0.000 000 000 135 523 893 6(3.7)	-0.000 000 000 064 880	70 643.
	20	-2.001 250 000 117 766 859 9(3)	-0.000 000 000 117 766 859 9(3.5)	-0.000 000 000 056 391	61 376.
	21	-2.001 133 786 950 972 664 2(3)	-0.000 000 000 102 900 101 8(3.2)	-0.000 000 000 049 265	53 635.

TABLE IV. Nonrelativistic energies for the high- L Rydberg states of helium. Units are atomic units.

L	n	E	L	n	E	L	n	E
8	9	-2.006 172 844 174 560 38(12)	12	13	-2.002 958 580 101 207 765 823(36)	14	15	-2.002 222 222 289 793 953 536 6(20)
	10	-2.005 000 003 675 244 49(13)		14	-2.002 551 020 594 708 187 804(59)		16	-2.001 953 125 058 721 907 548 7(34)
	11	-2.004 132 234 317 414 12(15)		15	-2.002 222 222 380 947 857 240(75)		17	-2.001 730 103 857 288 827 819 4(43)
	12	-2.003 472 224 554 125 18(14)		16	-2.001 953 125 135 545 320 024(83)		18	-2.001 543 209 921 042 675 294 9(49)
	13	-2.002 958 581 769 974 76(14)		17	-2.001 730 103 922 521 924 511(86)		19	-2.001 385 041 590 151 707 230 9(53)
	14	-2.002 551 021 954 497 07(13)		18	-2.001 543 209 976 832 911 265(86)		20	-2.001 250 000 034 138 563 390 0(54)
	15	-2.002 222 223 502 038 82(12)		19	-2.001 385 041 638 190 382 080(84)		21	-2.001 133 786 878 144 252 243 7(54)
	16	-2.001 953 126 069 770 01(11)		20	-2.001 250 000 075 766 338 519(80)		22	-2.001 033 057 877 832 623 732 1(52)
	17	-2.001 730 104 708 628 24(9)		21	-2.001 133 786 914 431 440 619(76)		23	-2.000 945 179 607 728 619 807 7(50)
	18	-2.001 543 210 644 174 53(8)		22	-2.001 033 057 909 639 997 850(70)		24	-2.000 868 055 576 592 020 687 4(48)
9	10	-2.005 000 001 934 675 381(8)	13	14	-2.002 551 020 527 347 779 223(8)	15	16	-2.001 953 125 039 779 842 387 5(6)
	11	-2.004 132 232 966 556 319(13)		15	-2.002 222 222 324 721 558 027(13)		17	-2.001 730 103 841 114 291 478 6(9)
	12	-2.003 472 223 488 347 173(16)		16	-2.001 953 125 088 231 855 907(17)		18	-2.001 543 209 907 146 937 774 8(12)
	13	-2.002 958 580 916 242 013(16)		17	-2.001 730 103 882 396 195 792(19)		19	-2.001 385 041 578 142 319 811 2(14)
	14	-2.002 551 021 261 123 416(16)		18	-2.001 543 209 942 549 970 092(20)		20	-2.001 250 000 023 699 812 584 4(15)
	15	-2.002 222 222 931 854 517(15)		19	-2.001 385 041 608 695 107 823(20)		21	-2.001 133 786 869 021 154 568 0(16)
	16	-2.001 953 125 595 605 871(14)		20	-2.001 250 000 050 224 898 230(20)		22	-2.001 033 057 869 818 201 744 0(16)
	17	-2.001 730 104 310 311 145(13)		21	-2.001 133 786 892 179 758 171(19)		23	-2.000 945 179 600 653 920 629 3(15)
	18	-2.001 543 210 306 503 564(12)		22	-2.001 033 057 890 145 057 527(19)		24	-2.000 868 055 570 318 325 084 2(15)
	19	-2.001 385 041 920 650 045(11)		23	-2.000 945 179 618 584 203 280(18)		25	-2.000 800 000 013 226 300 964 2(14)

relativistic corrections, and quantum electrodynamic corrections [10,13,18,19]. However, there is no point in including these terms until the existing discrepancy between the AE and CI results for the nonrelativistic energy is resolved. It may be that the discrepancy is pointing to an important class of configurations that has not been included in the CI calculations. For example, in Hylleraas coordinates, the variational basis set does not become asymptotically complete unless one includes all the angular momentum couplings $\mathbf{l}_1+\mathbf{l}_2=\mathbf{L}$ with $(l_1, l_2; L) = (0, L; L), (1, L-1; L), \dots, ([L/2], L-[L/2]; L)$, where [...] denotes “greatest integer in.” Analogous classes of terms are similarly important for more complex atomic systems.

After completion of this work, B. Piraux and co-workers [20] reported that in their CI calculations, they used the same

basis sets for $L > 7$ as for $L = 7$, and that this truncation accounts for the discrepancy. They confirmed that their results come into agreement to 15 figures when couplings involving higher angular momenta are included. This demonstrates the important role played by high angular momentum couplings in capturing an adequate representation of the core polarization effects beyond the screened hydrogenic term.

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- [1] G. Lagmago Kamta, B. Piraux, and A. Scrinzi, Phys. Rev. A **63**, 040502(R) (2001).
 [2] C. Schwartz, Int. J. Mod. Phys. E **15**, 877 (2006).
 [3] H. Nakashima and H. Nakatsuji, J. Chem. Phys. **127**, 224104 (2007).
 [4] H. Nakashima, Y. Hijikata, and H. Nakatsuji, J. Chem. Phys. **128**, 154108 (2008).
 [5] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **11**, 1479 (1975) and earlier references therein.
 [6] G. D. Stevens and S. R. Lundeen, Phys. Rev. A **60**, 4379 (1999).
 [7] S. R. Lundeen, Adv. At., Mol., Opt. Phys. **52**, 161 (2005).
 [8] G. W. F. Drake and Z.-C. Yan, Phys. Rev. A **46**, 2378 (1992).
 [9] G. W. F. Drake, in *Long Range Casimir Forces: Theory and Recent Experiments on Atomic Systems*, edited by F. S. Levin and D. Micha (Plenum, New York, 1993), pp. 107–217.
 [10] G. W. F. Drake, Adv. At., Mol., Opt. Phys. **31**, 1 (1993).
 [11] G. W. F. Drake, Adv. At., Mol., Opt. Phys. **32**, 93 (1993).
 [12] R. J. Drachman, Phys. Rev. A **26**, 1228 (1982).
 [13] R. J. Drachman, in *Long Range Casimir Forces: Theory and Recent Experiments on Atomic Systems*, edited by F. S. Levin and D. Micha (Plenum, New York, 1993), pp. 219–272.
 [14] G. W. F. Drake, Phys. Rev. A **45**, 70 (1992).
 [15] R. J. Drachman, in *Long Range Casimir Forces: Theory and Recent Experiments on Atomic Systems*, edited by F. S. Levin and D. Micha (Plenum, New York, 1993).
 [16] G. W. F. Drake and R. A. Swainson, Phys. Rev. A **42**, 1123 (1990).
 [17] R. A. Swainson and G. W. F. Drake, Can. J. Phys. **70**, 187 (1992).
 [18] R. J. Drachman, Phys. Rev. A **37**, 979 (1988).
 [19] G. W. F. Drake and Z.-C. Yan, Can. J. Phys. **86**, 45 (2008).
 [20] J. Eiglsperger, B. Piraux, and J. Madroño, Phys. Rev. A **80**, 022511 (2009); private communication.