Polarizabilities of the Rydberg states of helium

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The static dipole, quadrupole, and octupole polarizabilities of helium are calculated for the four Rydberg series 1sns ^{1}S , 1sns ^{3}S , 1snp ^{1}P , and 1snp ^{3}P with n up to 10, using variational wave functions in Hylleraas coordinates. The large-n expansions for polarizabilities are presented for these series.

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I. INTRODUCTION

Recently, a series of high-precision work [1-6] has been done for the calculations of polarizabilities and dispersion coefficients for helium and heliumlike ions. However, all these calculations are limited to the ground state $1s^2$ S, the metastable 1s2s ^{1}S and 1s2s ^{3}S states, and the lowest Pstates 1s2p ^{1}P and 1s2p ^{3}P . On the other hand, polarizabilities of an atom in Rydberg states are important in the studies of threshold behavior of photodetachment cross sections for negative ions such as He⁻, Li⁻, Na⁻, and K⁻ [7]. The recent experimental work by Kiyan et al. [8] on the doubly excited states of He has shown that the polarizabilities of excited states of the parent atom He are crucial in the determination of the number of bound states below a particular excited state of the parent atom. However, for helium Rydberg states, to our knowledge, there have been no precision calculations of polarizabilities reported in the literature. The purpose of this paper is to present accurate values of polarizabilities for Rydberg series of helium using fully correlated Hylleraas variational basis sets.

II. CALCULATIONS

The static 2^l -pole polarizability for an atom is defined in terms of a sum over all intermediate states, including the continuum (in atomic units throughout):

$$\alpha_l = \sum_{n \neq 0} \frac{f_{n0}^{(l)}}{(E_n - E_0)^2},\tag{1}$$

with $f_{n0}^{(l)}$ being the 2^{l} -pole oscillator strength

$$f_{n0}^{(l)} = \frac{8\pi}{2l+1} (E_n - E_0) \left| \left\langle \Psi_0 \middle| \sum_i r_i^l Y_{lm}(\hat{\mathbf{r}}_i) \middle| \Psi_n \right\rangle \right|^2, \quad (2)$$

where the sum i runs over all the electrons in the atom, Ψ_0 is the state of interest, E_0 is the corresponding energy, and Ψ_n is one of the intermediate states with the associated energy eigenvalue E_n . In practice, instead of $f_{n0}^{(l)}$, an averaged oscillator strength $\overline{f}_{n0}^{(l)}$ which is independent of magnetic quantum number m is used. The $\overline{f}_{n0}^{(l)}$ is obtained by averaging over the initial-state orientation degeneracy and summing over the final-state degeneracy. It is convenient to introduce reduced matrix elements through the Wigner-Eckart theorem [9]

$$\langle \gamma' L' M' | \sum_{i} r_{i}^{l} Y_{lm}(\hat{\mathbf{r}}_{i}) | \gamma L M \rangle$$

$$= (-1)^{L' - M'} \begin{pmatrix} L' & l & L \\ -M' & m & M \end{pmatrix}$$

$$\times \langle \gamma' L' | \left| \sum_{i} r_{i}^{l} Y_{l}(\hat{\mathbf{r}}_{i}) \right| | \gamma L \rangle. \tag{3}$$

With the aid of a sum rule for the 3j symbols, we have

$$\overline{f}_{n0}^{(l)} = \frac{8\pi}{(2l+1)^2 (2L_0+1)} (E_n - E_0)
\times \left| \left\langle \Psi_0 \right| \left| \sum_i r_i^l Y_l(\hat{\mathbf{r}}_i) \right| \left| \Psi_n \right\rangle \right|^2,$$
(4)

where L_0 is the total angular momentum for the initial state (the state of interest). The allowed possible symmetries of intermediate states can be obtained by the selection rules of the 3j symbol and parity. Thus, if the symmetry of the initial state is S, then the allowed symmetries are P, D, and F for the dipole, quadrupole, and octupole polarizabilities, respectively; if the symmetry of the initial state is P, then the allowed symmetries are S+P+D, P+D+F, and D+F+G respectively. A more detailed discussion on the construction of configurations for the intermediate states can be found in Ref. [6]. It should be pointed out that in the latter case one of the intermediate states of P symmetry, which overlaps with the initial state, should be excluded in the summation over n in Eq. (1).

One difference between a Rydberg state and the ground state (and metastable states as well) is that not all the virtual excitation energies $E_n - E_0$ are positive for the Rydberg state. Let Ψ_0 be a Rydberg state and all the intermediate states of correct symmetry below Ψ_0 be $\{\phi_i\}_{i=1}^g$. One approach is to calculate the contributions to the polarizabilities from ϕ_i explicitly and to treat the contributions from the states above Ψ_0 , including the continuum, by diagonalizing the Hamiltonian in a restricted basis set,

$$\left(1 - \sum_{i=1}^{g} |\phi_i\rangle\langle\phi_i|\right) \times (\text{basis function}). \tag{5}$$

The resulting eigenvalues are all above the energy of the initial state and the problem thus becomes similar to the problem for the ground-state case. This method works well for low-lying states. For instance, consider the $1 s 3 s \, ^1 S$ state.

For the calculation of dipole polarizability α_1 , the only state of P symmetry which is below $1s3s^{-1}S$ is the state of $|\phi_1\rangle = |1s2p^{-1}P\rangle$. The contribution to α_1 from ϕ_1 can be calculated directly and the value is $-37.155\,811\,9(5)$. After diagonalizing the Hamiltonian in a restricted functional space Eq. (5), one obtains the contribution from all the states above $1s3s^{-1}S$ to be $16\,924.31(2)$. Combining these two contributions together yields the total α_1 of $16\,887.15(2)$. For highlying states, however, where $\{\phi_i\}_{i=1}^g$ becomes more complete, the gram matrix becomes more singular, leading eventually to numerical instabilities. Therefore, the strategy we adopt is to diagonalize the Hamiltonian directly without using projection operators. The reliability of the method can be judged by the convergence pattern as the size of basis set for a given intermediate symmetry increases progressively.

For a two-electron atomic system, the basis set is constructed using Hylleraas coordinates

$$\{\chi_{ijk} = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1 l_2}^{LM}(\mathbf{r}_1, \mathbf{r}_2)\}, \tag{6}$$

where $\mathcal{Y}_{l_1 l_2}^{LM}(\mathbf{r}_1, \mathbf{r}_2)$ is the vector coupled product of solid spherical harmonics for the two electrons forming an eigenstate of total angular momentum L defined by

$$\mathcal{Y}_{l_{1}l_{2}}^{LM}(\mathbf{r}_{1},\mathbf{r}_{2}) = \sum_{m_{1}m_{2}} \langle l_{1}l_{2}m_{1}m_{2}|LM\rangle Y_{l_{1}m_{1}}(\mathbf{r}_{1})Y_{l_{2}m_{2}}(\mathbf{r}_{2}),$$

$$(7)$$

and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between electron 1 and 2. The wave functions are expanded from doubled basis sets. The explicit form for the wave function is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ijk} \left[a_{ijk}^{(1)} \chi_{ijk}(\alpha_1, \beta_1) + a_{ijk}^{(2)} \chi_{ijk}(\alpha_2, \beta_2) \right]$$

$$\pm (\text{exchange}), \tag{8}$$

and $i+j+k \le \Omega$. A complete optimization is then performed with respect to the two sets of nonlinear parameters α_1 , β_1 , and α_2 , β_2 by first calculating the derivatives analytically in

$$\frac{\partial E}{\partial \gamma} = 2 \left\langle \Psi \middle| H \middle| \frac{\partial \Psi}{\partial \gamma} \middle\rangle - 2E \left\langle \Psi \middle| \frac{\partial \Psi}{\partial \gamma} \middle\rangle, \tag{9}$$

where γ represents any nonlinear parameter, E is the trial energy, H is the Hamiltonian, and $\langle \Psi | \Psi \rangle = 1$ is assumed, and then locating the zeros of the derivatives by Newton's method. These techniques yield much improved convergence relative to single basis-set calculations [10]. The energy eigenvalues for the Rydberg series 1sns and 1snp are accurate to about 12 to 15 significant figures, for the largest sizes of basis sets around 500 for the 1sns series and 800 for the 1snp series. For the intermediate states of given symmetry, the nonlinear parameters are optimized such that the energy eigenvalue closest to the energy of initial state E_0 is minimized.

The basic integrals that appear in our variational calculations are of the form

$$I(a,b,c;\alpha,\beta) = \int d\mathbf{r}_1 d\mathbf{r}_2 \mathcal{Y}_{l_1'l_2'}^{L'M'}(\mathbf{r}_1,\mathbf{r}_2) * \mathcal{Y}_{l_1l_2}^{LM}(\mathbf{r}_1,\mathbf{r}_2)$$
$$\times r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2}. \tag{10}$$

For the nonrelativistic eigenvalue problem, it is only necessary to consider the case of $c \ge -1$ in Eq. (10). Equation (10) can be decoupled by first expanding r_{12} [11],

$$r_{12}^{c} = \sum_{q=0}^{L_{1}} P_{q}(\cos \theta_{12}) \sum_{k=0}^{L_{2}} C_{cqk} r_{<}^{q+2k} r_{>}^{c-q-2k}, \quad (11)$$

where $r_<=\min(r_1,r_2)$ and $r_>=\max(r_1,r_2)$. For $c \ge -1$, for even values of c, $L_1=\frac{1}{2}c$, $L_2=\frac{1}{2}c-q$; for odd values of c, $L_1=\infty$, $L_2=\frac{1}{2}(c+1)$. Also in Eq. (11), the coefficients are given by

$$C_{cqk} = \frac{2q+1}{c+2} {c+2 \choose 2k+1} \prod_{t=0}^{S_{qc}} \frac{2k+2t-c}{2k+2q-2t+1}, \quad (12)$$

where $S_{qc} = \min[q-1,\frac{1}{2}(c+1)]$. Then after applying the addition theorem for spherical harmonics,

$$P_{q}(\cos\theta_{12}) = \frac{4\pi}{2q+1} \sum_{m=-q}^{q} Y_{qm}(\hat{\mathbf{r}}_{1}) * Y_{qm}(\hat{\mathbf{r}}_{2}), \quad (13)$$

we can arrive at the final result

$$I(a,b,c;\alpha,\beta) = \sum_{q,k} C_{cqk} G(q) I_{\mathbb{R}}(a,b,c;\alpha,\beta;q,k),$$

$$\tag{14}$$

where the angular part G(q) is

$$G(q) = (-1)^{L+q} (l_1, l_2, l'_1, l'_2)^{1/2} \begin{pmatrix} l'_1 & l_1 & q \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_2 & l_2 & q \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{Bmatrix} L & l_1 & l_2 \\ q & l'_2 & l'_1 \end{Bmatrix} \delta_{MM'} \delta_{LL'}, \qquad (15)$$

and the radial part I_R is

$$I_{R}(a,b,c;\alpha,\beta;q,k)$$

$$= \frac{s!}{(\alpha+\beta)^{s+1}} \left[\frac{1}{a+3+q+2k} \times {}_{2}F_{1} \left(1,s+1;a+4+q+2k; \frac{\alpha}{\alpha+\beta} \right) + \frac{1}{b+3+q+2k} \times {}_{2}F_{1} \left(1,s+1;b+4+q+2k; \frac{\beta}{\alpha+\beta} \right) \right], \tag{16}$$

where ${}_{2}F_{1}(a,b;c;x)$ is the hypergeometric function, and s=a+b+c+5. Further details can be found in Ref. [12]. It should be pointed out that in Eq. (14) the range of q is limited by the triangular rule of the 3-j symbols in Eq. (15),

TABLE I. Convergence of the contributions to the dipole polarizability of 1s4p 3P from the S, P, and D symmetries with respect to the sizes of basis sets N_P , N_S , N_{PP} , and N_D , where N_P is for 1s4p 3P , and N_S , N_{PP} , and N_D are for the three intermediate symmetries. Units are a.u.

N_P	N_S	N_{PP}	N_D	$\alpha_1(^3S)$	$\alpha_1((pp')^3P)$	$\alpha_1(^3D)$
405	264	504	390	-20555.20497	0.067 5	190 945.036
516	330	616	509	-20555.20487	0.0709	190 945.049
644	405	744	649	-20555.20483	0.0769	190 945.056
790	490	888	811	-20555.20460	0.0796	190 945.066

$$q_m \leqslant q \leqslant q_M, \tag{17}$$

where

$$q_m = \max(|l_1 - l_1'|, |l_2 - l_2'|), \tag{18}$$

$$q_{M} = \min(l_{1} + l'_{1}, l_{2} + l'_{2}). \tag{19}$$

Thus, the summation over q in Eq. (14) is always finite even when c is odd.

III. RESULTS

Table I contains a typical convergence pattern for the contributions to the dipole polarizability of $1s4p^3P$ from the three intermediate 3S , 3P , and 3D symmetries, where 3P is from the doubly excited (pp') configuration. Tables II and III list the values of the polarizabilities α_1 , α_2 , and α_3 for the Rydberg series of $1sns^1S$, $1sns^3S$, $1snp^1P$, and $1snp^3P$ with n up to 10. For the sake of completeness,

we have also included the results for the two metastable states [2] $1s2s^1S$ and $1s2s^3S$, as well as for the lowest P states [6] $1s2p^1P$ and $1s2p^3P$. A comprehensive comparison for the metastable states can be found in Ref. [2]. The contributions from doubly excited configurations are negligibly small for $n \ge 4$. The dipole polarizabilities derived by Kiyan *et al.* [8] from a photodetachment experiment of He are 147 392 for $1s4p^3P$ and 1 389 170 for $1s5p^3P$. The discrepancies between their values and the present ones are 15% and 35%, respectively, almost the same as what they have estimated.

The polarizabilities of states with n higher than 10 are estimated by extrapolation. The leading asymptotic form has been found to be $\alpha_l \sim n^{4l+3}$, except for the octupole polarizabilities of P states where the contribution from the G symmetry seems to obey the power law n^p , where $p \sim 17$ or 18, instead of 15. This problem needs to be further investigated. This power law also does not apply to hydrogen [13], since the correct power law for the dipole polarizability of hydrogen is n^6 , rather than n^7 . The extrapolated results for He are

$$\alpha_1(n^1S) = 9.119\ 20(14)n^7 - 0.168\ 99(36)n^6$$

$$-14.144\ 23(80)n^5 + 6.629\ 5(13)n^4$$

$$-1.233\ 0(90)n^3,$$

$$\alpha_1(n^3S) = 5.4025182(27)n^7 - 2.4680136(63)n^6$$
$$-12.926768(64)n^5 + 15.070(15)n^4$$
$$-5.782(44)n^3 - 0.945(88)n^2,$$

TABLE II. Values of the static polarizabilities α_1 , α_2 , and α_3 of helium in S states. Numbers in parentheses represent the estimated error in the last digit of the listed values. Units are a.u.

State	$lpha_1$	$lpha_2$	$lpha_3$
$\frac{1}{2} S$	$8.003\ 163\ 3(7)\times10^2$	$7.1060537(5)\times10^3$	$2.9370350(6)\times10^{5}$
2^3S	$3.1563147(1)\times10^2$	$2.7078773(3)\times10^{3}$	$8.83773253(7)\times10^4$
$3 {}^{1}S$	$1.688717(1) \times 10^4$	$1.64220535(2)\times10^6$	$1.265947(5) \times 10^{8}$
3^3S	$7.93758(1) \times 10^3$	$6.0842945(3)\times10^5$	$5.501\ 232\ 10(4) \times 10^7$
$4^{1}S$	$1.35851430(1)\times10^5$	$5.14513668(3)\times10^7$	$1.7985860(3)\times10^{10}$
4^3S	$6.8650061(2)\times10^4$	$1.938308499(1) \times 10^7$	$7.3952178(3)\times10^9$
$5^{-1}S$	$6.695858982(2)\times10^{5}$	$6.7753678(3)\times10^{8}$	$6.928708(3) \times 10^{11}$
5^3S	$3.51796060(2)\times10^{5}$	$2.571839250(2) \times 10^{8}$	$2.8091258(3)\times10^{11}$
$6^{1}S$	$2.443248402(4) \times 10^6$	$5.3755389(2)\times10^9$	$1.2539990(6) \times 10^{13}$
6^3S	$1.314954806(3) \times 10^6$	$2.044651220(2) \times 10^9$	$5.0557379(5) \times 10^{12}$
$7^{-1}S$	$7.2679455(5) \times 10^6$	$3.04667053(1) \times 10^{10}$	$1.3923951(7)\times10^{14}$
7^3S	$3.975757687(3) \times 10^6$	$1.157979718(3) \times 10^{10}$	$5.5894738(4)\times10^{13}$
$8^{1}S$	$1.864310000(5) \times 10^7$	$1.3572798(3)\times10^{11}$	$1.096328(4) \times 10^{15}$
8^3S	$1.03180706(3)\times10^7$	$5.1479399(2)\times10^{10}$	$4.3819370(1)\times10^{14}$
$9 {}^{1}S$	$4.2734453(1)\times10^7$	$5.04409020(5)\times10^{11}$	$6.682733(1) \times 10^{15}$
$9^{3}S$	$2.38597670(3) \times 10^7$	$1.90793490(3) \times 10^{11}$	$2.6591476(5)\times10^{15}$
$10^{1}S$	$8.967369(1)\times10^7$	$1.627015(3)\times10^{12}$	$3.34035(5) \times 10^{16}$
$10^{3}S$	$5.040935(1)\times10^7$	$6.135950(2) \times 10^{11}$	$1.323170(2)\times10^{16}$

TABLE III.	Values of	the static	polarizabilities	$\alpha_1, \alpha_2,$	and α_3	of heliun	n in P	states.	Numbers	in
parentheses repr	esent the es	stimated e	rror in the last d	igit of the	e listed	values. Ur	its are	a.u.		

State	$lpha_1$	$lpha_2$	$lpha_3$
$2^{1}P$	$-6.00285140(2)\times10^{1}$	$5.48267095(5)\times10^{3}$	$4.7345635(2)\times10^5$
$2^{3}P$	$4.67077482(3) \times 10^{1}$	$3.62279034(2)\times10^3$	$2.722\ 125\ 8(2) \times 10^5$
$3^{1}P$	$-9.7907993(4)\times10^{4}$	$5.842515(5) \times 10^5$	$-1.01667481(6)\times10^{9}$
$3^{3}P$	$1.7305598(3)\times10^4$	$4.2746155(5)\times10^5$	$2.9549840(5)\times10^{8}$
$4^{1}P$	$-9.4392388(5)\times10^{5}$	$-1.63012080(2)\times10^{8}$	$-1.14012156(1)\times10^{11}$
$4^{3}P$	$1.7038998(4)\times10^{5}$	$3.79229456(4) \times 10^7$	$3.0165426(5)\times10^{10}$
$5^{1}P$	$-4.94533455(6)\times10^6$	$-3.1476175(6)\times10^9$	$-5.3717303(1)\times10^{12}$
$5^{3}P$	$9.00120816(3)\times10^5$	$6.44344265(1)\times10^8$	$1.220941599(2)\times10^{12}$
$6^{1}P$	$-1.85715485(6)\times10^{7}$	$-2.89933117(2) \times 10^{10}$	$-1.09395634(1)\times10^{14}$
$6^{3}P$	$3.392252880(2) \times 10^6$	$5.70733525(3)\times10^9$	$2.3317365(5) \times 10^{13}$
$7^{-1}P$	$-5.6137425(2)\times10^{7}$	$-1.77481528(2) \times 10^{11}$	$-1.300511282(5)\times10^{15}$
$7^{3}P$	$1.026954840(2) \times 10^7$	$3.4302432(2)\times10^{10}$	$2.6862828(3)\times10^{14}$
$8^{1}P$	$-1.45432743(5)\times10^{8}$	$-8.27733875(5) \times 10^{11}$	$-1.068757194(2) \times 10^{16}$
$8^{3}P$	$2.66200085(5)\times10^7$	$1.5829125(1)\times10^{11}$	$2.16874072(3) \times 10^{15}$
$9^{1}P$	$-3.355674(5) \times 10^{8}$	$-3.1691170(1)\times10^{12}$	$-6.704807(1)\times10^{16}$
$9^{3}P$	$6.14281430(1)\times10^7$	$6.0183969(3)\times10^{11}$	$1.345477(2) \times 10^{16}$
$10^{1}P$	$-7.074025(3) \times 10^{8}$	$-1.0435045(3)\times10^{13}$	$-3.420460(4)\times10^{17}$
$10^{3}P$	$1.2947615(3)\times10^{8}$	$1.971875(2) \times 10^{12}$	$6.81236(6) \times 10^{16}$

$$\alpha_{2}(n^{1}S) = 17.0224(28)n^{11} + 2.6924(10)n^{10}$$

$$-111.266(17)n^{9} + 85.355(36)n^{8}$$

$$+62.292(60)n^{7} - 52.75(40)n^{6},$$

$$\alpha_{2}(n^{3}S) = 5.94570(14)n^{11} + 9.49031(36)n^{10}$$

$$-88.58770(78)n^{9} + 133.3214(13)n^{8}$$

$$-62.3127(20)n^{7},$$

$$\alpha_{3}(n^{1}S) = 36.546(42)n^{15} + 29.978(51)n^{14}$$

$$-732.212(48)n^{13} + 1180.76(40)n^{12},$$

$$\alpha_{3}(n^{3}S) = 12.926(56)n^{15} + 39.890(68)n^{14}$$

$$-444.536(64)n^{13} + 761.64(52)n^{12},$$

$$\alpha_{1}(n^{1}P) = -73.34451(73)n^{7} + 2.8632(15)n^{6}$$

$$+227.4752(28)n^{5} + 47.3679(46)n^{4}$$

$$-80.1572(58)n^{3} + 380.866(41)n^{2},$$

$$\alpha_{1}(n^{3}P) = 13.26967(50)n^{7} + 2.44320(70)n^{6}$$

$$-57.69732(90)n^{5} + 12.3010(70)n^{4}$$

$$-17.0521(80)n^{3},$$

$$\alpha_{2}(n^{1}P) = -119.432(28)n^{11} + 5.786(57)n^{10}$$

 $+1494.54(10)n^9 - 180.33(17)n^8$ $-2400.66(22)n^7 - 2142(2)n^6$,

$$\alpha_2(n^3P) = 21.76339(12)n^{11} + 7.27630(20)n^{10}$$

- 291.69456(29) $n^9 + 83.65086(32)n^8$
+ 610.0553(24) n^7 .

From the above expressions one can see that the polarizabilities for the $1sns^1S$, $1sns^3S$, and $1snp^3P$ series are positive, whereas the polarizabilities for the $1snp^1P$ series are asymptotically negative. Table IV gives a comparison of polarizabilities between the directly calculated values and the values predicted by the above formulas for the states of n=13. The agreement is excellent for α_1 for the S states and for the 13^1P state. For 13^3P , the percentage difference is 0.4%. For α_2 , the largest discrepancy is at the 2% level for the 13^3P state.

TABLE IV. Comparison of polarizabilities between the directly calculated values (the first entry) and the values predicted by the asymptotic formulas (the second entry) for the states of n=13. Units are a.u.

State	α_1	$lpha_2$	α_3
13 ¹ S	$5.663\ 355\ 86 \times 10^{8}$	2.9558×10^{13}	1.740×10^{18}
	5.66335576×10^{8}	$2.977.1 \times 10^{13}$	1.794×10^{18}
$13^{3}S$	3.2270527×10^{8}	1.1054×10^{13}	6.749×10^{17}
	3.2270530×10^{8}	1.1129×10^{13}	7.017×10^{17}
$13 {}^{1}P$	-4.50307×10^{9}	-1.97859×10^{14}	
	-4.50273×10^{9}	-1.97703×10^{14}	
$13^{3}P$	8.1997×10^{8}	3.6289×10^{13}	
	8.2333×10^{8}	3.7019×10^{13}	

In summary, accurate Hylleraas basis sets have been applied to the calculations of polarizabilities α_1 , α_2 , and α_3 for the Rydberg series of helium 1sns 1S , 1sns 3S , 1snp 1P , and 1snp 3P , with n up to 10. We hope that the reliability of our data will be confirmed by other independent calculations.

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