Expectation values of r^P for arbitrary hydrogenic states

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Expectation values of r^P for an arbitrary nl hydrogenic state are expressed in terms of state-independent coefficients that are determined by a simple recursion relation. Explicit results are given for negative P down to -16 and, by an algebraic transformation, for positive P up to 13. Closed-form expressions are obtained for the coefficients of the two highest-order terms in l multiplying each power of n. The result is an asymptotic expression valid for each P and sufficiently large l.

I. INTRODUCTION

The derivation of general expressions for expectation values of r^P with respect to hydrogen-atom wave functions has a long history, beginning with the early work of Waller,[1] Van Vleck,[2] and Pasternak.[3] Here, P is a positive or negative integer and r is the radial coordinate. Such general expressions are particularly important in asymptotic expansions for the energy and other atomic properties of Rydberg atoms consisting of an electron in a high-nl quantum state moving in the field of a polarizable core. For example, the ionization energy of the Rydberg electron is given by the well-known expansion[4]

$$-\Delta E=\alpha_1\langle r^{-4}\rangle+(\alpha_2-6\beta_1)\langle r^{-6}\rangle+\cdots\ \mathrm{Ry}\ , \tag{1}$$

where α_1 is the dipole polarizability, α_2 is the quadrupole polarizability, β_1 is the leading nonadiabatic correction etc., and the expectation value is with respect to the Rydberg electron.

The terms in Eq. (1) are currently known in their entirety up to $\langle r^{-8}\rangle$.[4] Recent advances in experimental precision for the Rydberg states of helium[5] and the accuracy that can be achieved in variational calculations[6] call for an extension of Eq. (1) to higher inverse powers. The most extensive tabulation of expectation values $\langle r^{-P}\rangle$ by Bockasten[7] gives general expressions as a function of n and l up to $P=8$. However, his method, which involves sums over triple products of binomial coefficients, is algebraically tedious and difficult to extend to higher powers. The purpose of this paper is to derive a simple recursion relation which allows one sequentially to obtain general expressions for any $\langle r^{-P}\rangle$ with a minimum of effort. Explicit results are given for all cases up to $P=16$.

II. MATHEMATICAL DERIVATION

We begin by observing that a general nonrelativistic expectation value $\langle r^{-P}\rangle$ for a one-electron atom with nuclear charge Z depends on n and l according to (in atomic units)

$$\langle nl|r^{-P}|nl\rangle=F_PG_P(n,l)\sum_{q=0}^{N}C_q^{(P)}n^{P-2q-2}\sum_{r=0}^{q}d_{q,r}^{(P)}f_r(l)\ , \tag{2}$$

where $N=[P/2]-1$ and $f_r(l)=(l+r)!/(l-r)!$ is a function only of l. The notation [ ] denotes "greatest integer in." The functional dependence on n and l in Eq. (2) follows from a theorem stated by Pasternak.[3] The quantities F_P, $G_P(n,l)$, and $C_q^{(P)}$ are chosen for convenience to be

$$F_P=\begin{cases}\dfrac{(P-3)!}{(P/2-1)!(P/2-2)!} & \text{for } P \text{ even}\\[2ex] \dfrac{(P-2)!}{[(P/2-3/2)!]^2} & \text{for } P \text{ odd}\ ,\end{cases} \tag{3}$$

$$G_P(n,l)=\frac{2^PZ^P(2l-P+2)!}{n^{P+1}(2l+P-1)!}\ , \tag{4}$$

$$C_q^{(P)}=\frac{N!2^{N-q}(-1)^q}{(P-2q-2)!q!}\prod_{s=q}^{N-1}(2P-2s-5)\ , \tag{5}$$

with $C_N^{(P)}=(-1)^N$ for all P. The above choices are suggested by the known results up to $P=8$. They yield a useful partial factorization of the final coefficients.

The remaining coefficients $d_{q,r}^{(P)}$ are determined by use of the Kramers-Pasternak recursion relation[8]

$$\langle r^{-P-2}\rangle=\frac{4}{(2l+P+1)(2l-P+1)}\times\left[\left(\frac{2P-1}{P}\right)Z\langle r^{-P-1}\rangle-\left(\frac{P-1}{n^2P}\right)Z^2\langle r^{-P}\rangle\right]\ . \tag{6}$$

Substituting Eqs. (2)–(5) into (6) and equating coefficients of equal powers of n and l yield the recursion relation

$$d_{q,r}^{(P+2)}=\frac{1}{P(2P-2q-1)}\left((P-2q)(2P-1)d_{q,r}^{(P+1)}+2q(P-1)\{d_{q-1,r-1}^{(P)}+[r(r+1)-\tfrac{1}{4}P(P-2)]d_{q-1,r}^{(P)}\}\right) \tag{7}$$

for $q=0,1,\ldots,N$ and $r=0,1,\ldots,q$, starting with the values

$d_{0,0}^{(2)}=1, \quad d_{0,0}^{(3)}=1$,

and coefficients with negative subscripts are taken to be zero. With these starting values, the recursion relation (7) has the properties that

$$d_{q,q}^{(P)}=1 , \tag{8}$$

$$d_{q,q-1}^{(P)}=-\frac{q}{12}(P-2q-2)(P+2q-3) \tag{9}$$

for all $P\geq 2$ and $q=0,1,\ldots,[P/2]-1$. The derivation of Eq. (7) requires at an intermediate step the use of the identity

$$(l-P/2+1)(l+P/2)f_r(l)=f_{r+1}(l)+[r(r+1)-\tfrac{1}{4}P(P-2)]f_r(l) . \tag{10}$$

Since the coefficients given in Eqs. (8) and (9) multiply the highest powers of l for each n, they determine the high-l (and therefore necessarily high n) dependence of the integrals for all P. The result is

$$\langle nl|r^{-P}|nl\rangle \simeq F_P G_P(n,l)\sum_{q=0}^{N} C_q(P)n^{P-2q-2}[f_q(l)-\frac{q}{12}(P-2q-2)(P+2q-3)f_{q-1}(l)] , \tag{11}$$

with F_P, $G_P(n,l)$, and $C_q^{(P)}$ as defined by Eqs. (3)–(5).

One could of course apply directly the recursion relation (6) to obtain sequentially the complete integrals for particular values of n and l. However, the aim of the core-polarization mode is to obtain (as far as possible) the asymptotic potential in a state-independent form. From this point of view, it is preferable to display and calculate separately the contribution from each inverse power of r. In addition, the $q=0$ and 1 terms of the asymptotic Eq. (11) completely determine the coefficients of the leading $1/n^3$ and $1/n^5$ terms in a $1/n$ expansion of the integrals. This, together with Eq. (1), gives the corresponding $1/n$ expansion of the polarization energies and associated quantum defects for Rydberg states.

The connection between matrix elements of positive and negative powers of r has been discussed by many authors.[3,9–14] For diagonal matrix elements, the result is

$$\langle nl|r^P|nl\rangle=\frac{(2l+P+2)!}{(2l-P-1)!}\left[\frac{n}{2Z}\right]^{2P+3}\langle nl|1/r^{P+3}|nl\rangle . \tag{12}$$

Substituting Eq. (2) into the right-hand side of (12) gives

$$\langle nl|r^P|nl\rangle=F_{P+3}\frac{n^{P-1}}{2^P Z^P}\sum_{q=0}^{\tilde N} C_q^{(P+3)}n^{P-2q+1} \times \sum_{r=0}^{q} d_{q,r}^{(P+3)}f_r(l) , \tag{13}$$

with $\tilde N=[(P+1)/2]$. This is identical in form to Eq. (2) except that the factor $G_{P+2}(n,l)$ has been replaced by $n^{P-1}/(2Z)^P$. Equation (13) is valid for all l, even though the right-hand side of (12) diverges for $l<\tilde N-1$. The asymptotic result corresponding to Eq. (11) is

$$\langle nl|r^P|nl\rangle \simeq F_{P+3}\frac{n^{P-1}}{2^P Z^P}\sum_{q=0}^{\tilde N} C_q^{(P+3)}n^{P-2q+1}[f_q(l)-\frac{q}{12}(P-2q+1)(P+2q)f_{q-1}(l)] . \tag{14}$$

III. RESULTS

To save manual labor and ensure accuracy, it is now a straightforward matter to program the recursion relation (7) and identify the numerical coefficients as rational fractions. There is never a problem of numerical cancellation because the three terms on the right-hand side of (7) are always of the same sign (or sum to zero for the terms $d_{N,r}^{(P)}$, $r=0,1,\ldots,N-1$ with P even). In addition, one knows that the product of the three coefficients F_P, $C_q^{(P)}$, and $d_{q,r}^{(P)}$ in (2) must always be an integer. With this in mind, the results are

$$\langle 1/r^2\rangle=G_2(n,l)/2 ,$$

$$\langle 1/r^3\rangle=nG_3(n,l) ,$$

$$\langle 1/r^4\rangle=G_4(n,l)[3n^2-f_1(l)] ,$$

$$\langle 1/r^5\rangle=6G_5(n,l)\{\tfrac{5}{3}n^3-n[f_1(l)-\tfrac{1}{3}]\} ,$$

$$\langle 1/r^6\rangle=3G_6(n,l)\{\tfrac{35}{3}n^4-10n^2[f_1(l)-\tfrac{5}{6}]+f_2(l)\} ,$$

$$\langle 1/r^7\rangle=30G_7(n,l)\{\tfrac{21}{5}n^5-\tfrac{14}{3}n^3[f_1(l)-\tfrac{3}{2}]+n[f_2(l)-\tfrac{4}{3}f_1(l)+\tfrac{4}{5}]\} ,$$

$$\langle 1/r^8\rangle = 10G_8(n,l)\{\tfrac{231}{5}n^6 - 63n^4[f_1(l)-\tfrac{7}{3}] + 21n^2[f_2(l)-3f_1(1)+\tfrac{14}{5}] - f_3(l)\}\ ,$$

$$\langle 1/r^9\rangle = 140G_9(n,l)\{\tfrac{429}{35}n^7 - \tfrac{99}{5}n^5[f_1(l)-\tfrac{10}{3}] + 9n^3[f_2(l)-5f_1(l)+\tfrac{101}{15}] - n[f_3(l)-3f_2(l)+\tfrac{36}{5}f_1(l)-\tfrac{36}{7}]\}\ ,$$

$$\begin{aligned}\langle 1/r^{10}\rangle = 35G_{10}(n,l)\{&\tfrac{1287}{7}n^8 - \tfrac{1716}{5}n^6[f_1(l)-\tfrac{9}{2}] + 198n^4[f_2(l)-\tfrac{22}{3}f_1(l)+\tfrac{27}{2}]\\ &-36n^2[f_3(l)-\tfrac{13}{2}f_2(l)+\tfrac{332}{15}f_1(l)-\tfrac{761}{35}] + f_4(l)\}\ ,\end{aligned}$$

$$\begin{aligned}\langle 1/r^{11}\rangle = 630G_{11}(n,l)\{&\tfrac{2431}{63}n^9 - \tfrac{572}{7}n^7[f_1(l)-\tfrac{35}{6}] + \tfrac{286}{5}n^5[f_2(l)-10f_1(l)+\tfrac{145}{6}]\\ &-\tfrac{44}{3}n^3[f_3(l)-\tfrac{21}{2}f_2(l)+48f_1(l)-\tfrac{1315}{21} + n[f_4(l)-\tfrac{16}{3}f_3(l)+\tfrac{144}{5}f_2(l)-\tfrac{576}{7}f_1(l)+64]\}\ ,\end{aligned}$$

$$\begin{aligned}\langle 1/r^{12}\rangle = 126G_{12}(n,l)\{&\tfrac{46\,189}{63}n^{10} - \tfrac{12\,155}{7}n^8[f_1(l)-\tfrac{22}{3}] + 1430n^6[f_2(l)-13f_1(l)+\tfrac{1199}{30}]\\ &-\tfrac{1430}{3}n^4[f_3(l)-15f_2(l)+\tfrac{177}{2}f_1(l)-\tfrac{3124}{21}]\\ &+55n[f_4(l)-\tfrac{34}{3}f_3(l)+84f_2(l)-\tfrac{2124}{7}f_2(l)+\tfrac{10\,736}{35}] - f_5(l)\}\ ,\end{aligned}$$

$$\begin{aligned}\langle 1/r^{13}\rangle = 2272G_{13}(n,l)\{&\tfrac{4199}{33}n^{11} - \tfrac{20\,995}{63}n^9[f_1(l)-9] + \tfrac{2210}{7}n^7[f_2(l)-\tfrac{49}{3}f_1(l)+\tfrac{623}{10}]\\ &-130n^5[f_3(l)-20f_2(l)+\tfrac{887}{6}f_1(l)-\tfrac{1873}{6}]\\ &+\tfrac{65}{3}n^3[f_4(l)-18f_3(l)+174f_2(l)-\tfrac{16\,372}{21}f_1(l)+\tfrac{35\,076}{35}]\\ &-n[f_5(l)-\tfrac{25}{3}f_4(l)+80f_3(l)-\tfrac{3600}{7}f_2(l)+1600f_1(l)-\tfrac{14\,400}{11}]\}\ ,\end{aligned}$$

$$\begin{aligned}\langle 1/r^{14}\rangle = 462G_{14}(n,l)\{&\tfrac{96\,577}{33}n^{12} - 8398n^{10}[f_1(l)-\tfrac{65}{6}] + \tfrac{62\,985}{7}n^8[f_2(l)-20f_1(l)+\tfrac{1391}{15}]\\ &-4420n^6[f_3(l)-\tfrac{51}{2}f_2(l)+\tfrac{2307}{10}f_1(l)-\tfrac{7189}{12}]\\ &+975n^4[f_4(l)-\tfrac{76}{3}f^3(l)+\tfrac{1541}{5}f_2(l)-\tfrac{5048}{3}f_1(l)+\tfrac{606\,164}{225}]\\ &-78n^2[f_5(l)-\tfrac{35}{2}f_4(l)+\tfrac{680}{3}f_3(l)-\tfrac{12\,510}{7}f_2(l)+\tfrac{46\,752}{7}f_1(l)-\tfrac{529\,360}{77}] + f_6(l)\}\ ,\end{aligned}$$

$$\begin{aligned}\langle 1/r^{15}\rangle = 12\,012G_{15}(n,l)\{&\tfrac{185\,725}{429}n^{13} - \tfrac{14\,858}{11}n^{11}[f_1(l)-\tfrac{77}{6}] + 1615n^9[f_2(l)-24f_1(l)+133]\\ &-\tfrac{6460}{7}n^7[f_3(l)-\tfrac{63}{2}f_2(l)+\tfrac{3423}{10}f_1(l)-\tfrac{64\,421}{60}]\\ &+255n^5[f_4(l)-\tfrac{100}{3}f_3(l)+497f_2(l)-\tfrac{9764}{3}f_1(l)+\tfrac{57\,344}{9}]\\ &-30n^3[f_5(l)-\tfrac{55}{2}f_4(l)+\tfrac{1372}{3}f_3(l)-\tfrac{13\,058}{3}f_2(l)+\tfrac{96\,888}{5}f_1(l)-\tfrac{1\,358\,056}{55}]\\ &+n[f_6(l)-12f_5(l)+180f_4(l)-\tfrac{14\,400}{7}f_3(l)+14\,400f_2(l)-\tfrac{518\,400}{11}f_1(l)+\tfrac{518\,400}{13}]\}\ ,\end{aligned}$$

$$\begin{aligned}\langle 1/r^{16}\rangle = 1716G_{16}(n,l)\{&\tfrac{1\,671\,525}{143}n^{14} - \tfrac{1\,300\,075}{33}n^{12}[f_1(l)-15] + 52\,003n^{10}[f_2(l)-\tfrac{85}{3}f_1(l)+185]\\ &-33\,915n^8[f_3(l)-38f_2(l)+\tfrac{1465}{3}f_1(l)-12\,755/7]\\ &+11\,305n^6[f_4(l)-42f_3(l)+\tfrac{3759}{5}f_2(l)-\tfrac{17\,473}{3}f_1(l)+13\,718]\\ &-1785^4[f_5(l)-\tfrac{115}{3}f_4(l)+791f_3(l)-\tfrac{26\,864}{3}f_2(l)+\tfrac{423\,260}{9}f_1(l)-\tfrac{2\,409\,320}{33}]\\ &+105n^2[f_6(l)-25f_5(l)+\tfrac{1502}{3}f_4(l)-6908f_3(l)+\tfrac{282\,288}{5}f_2(l)\\ &\quad-\tfrac{2\,372\,512}{11}f_1(l)+\tfrac{224\,972\,736}{1001}] - f_7(l)\}\ .\end{aligned}$$

The above equations agree with those given by Bockasten[7] up to $P=8$. The presentation is slightly different from the usual format in that the powers of n are all even for P even and odd for P odd, with an extra factor of $1/n$ being absorbed into $G_P(n,l)$ for P odd. This is done so that the recursion relation assumes the same form for both P even and P odd. The results show the usefulness of the factorization that has been achieved, with the denominators being at most products of small prime numbers.

The total coefficients of $n^{P-2q-1}f_r(l)$ have been checked by calculating directly the matrix elements of $1/r^P$ for a sufficiently large triangular array of n and l values, and fitting the results of the functional form of Eq. (2). The results agree to within the accuracy of the numerical fitting (at least seven significant figures for P up to 13).

The corresponding equation for $\langle r^P\rangle$ can be read off directly from the above $\langle 1/r^{P+3}\rangle$ result, provided that the $G_{P+3}(n,l)$ factor is replaced by $n^{P-1}/(2Z)^P$. For example, $\langle 1/r^5 \rangle$ gives

$$\langle r^2 \rangle = 6(N/4Z^2)\{\tfrac{5}{3}n^3 - n[f_1(l) - \tfrac{1}{3}]\} \ . \tag{15}$$

In summary, we have considerably extended the range of powers for which the diagonal matrix elements of r^P and $1/r^P$ are known as an explicit function of n and l, and have given a recursion relation by which the range can easily be extended further. The asymptotic expression (11) completely determines the coefficients of the leading $1/n^3$ and $1/n^5$ terms in a $1/n$ expansion of the integrals. It is hoped that the results presented here will provide a useful tabulation in the study of Rydberg atoms.

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