PHYSICAL REVIEW A VOLUME 39, NUMBER 5 MARCH 1, 1989

Alternative forms of the Coulomb approximation for bound-bound multipole transitions

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(Received 7 September 1988)

We discuss three different formulations of the Coulomb approximation that allow us to avoid numerical difficulties encountered with the standard one in the case of transitions between highly excited states. A common feature of these alternative (though not equivalent) methods is the fact that the radial multipole matrix elements are expressed in terms of standard or generalized hypergeometric functions. The recurrence relations satisfied by the latter can be used to bypass the loss of accuracy resulting from dramatic cancellations among their individual terms.

I. INTRODUCTION

Radiative transitions between high Rydberg states in nonhydrogenic atoms are a matter of considerable interest for astrophysics and atomic spectroscopy. The much celebrated Coulomb approximation (CA), introduced independently by Hylleraas,[1] and by Bates and Damgaard,[2] is ideally suited for calculating radial dipole or multipole matrix elements for such transitions. Unfortunately, the traditional analytical method,[2-5] which consists of using truncated asymptotic expansions for both Whittaker functions in the radial integral (RI), gets in trouble for effective principal quantum numbers $\nu,\nu' > 20$. Numerical integration has been used with some success to extend the range of previous tabulations,[6,7] but could not be applied beyond $\nu,\nu' \simeq 35$. This provides, however, the basis for a simple empirical extrapolation formula,[8,9] which is quite accurate for transitions with large ν,ν', and moderate $|\nu-\nu'|$. Similar formulas have been obtained subsequently by using the WKB approximation.[10,11]

A semianalytical approach that works nicely even for very high Rydberg states has been devised recently by van Regemorter and co-workers.[12,13] It is based, like the initial Bates-Damgaard tabulation, on linear interpolation of a smooth function of $\nu-\nu'$, and requires the evaluation of two bracketing RI in which one of the effective principal quantum numbers is an integer. The main point of the new method lies in the fact that the latter are expressed in closed form in terms of a finite number of hypergeometric functions (in fact polynomials), thus allowing a quick and accurate numerical calculation of the final result.

This paper describes three different methods for obtaining directly (i.e., without interpolation) good estimates of any dipole or multipole RI. In Sec. II we first show that the formula of van Regemorter *et al.* can be derived simply by rearranging the double-summation formula of Bates and Damgaard. This procedure is then extended to the case of arbitrary noninteger ν,ν' by introducing certain generalized hypergeometric polynomials.[14] An alternative strategy, developed in Sec. III, is based on employing for one of the states involved an exact integral representation, rather than its asymptotic expansion, in a manner similar to Hylleraas.[1] The resulting formula for the RI exhibits a number of quite remarkable features, and justifies, in particular, the use of hydrogenlike expressions for several important quantities. In Sec. IV we apply the so-called orbital quantum defect method,[15,16] in which the atomic states are described by regular wave functions obtained by slightly modifying the angular momenta. Although for low ν,ν' this method deviates in some cases quite strongly from the usual CA, it appears to be perfectly reliable for transitions between highly excited levels. Sample numerical results are discussed in Sec. V, and the conclusions presented in Sec. VI. Finally, the Appendix contains the derivation of a recurrence relation satisfied by the generalized hypergeometric polynomials used in Sec. II.

Throughout we use atomic units and restrict for simplicity to neutral atoms (net charge $z=1$). Formulas for transitions in positive ions are easily obtained by scaling.

II. REARRANGING THE DOUBLE ASYMPTOTIC FORMULA

The general RI to be evaluated reads

$$R_s=\langle \nu l|r^s|\nu' l'\rangle=\int_0^\infty dr\, P_{\nu l} r^s P_{\nu' l'} \ , \tag{1}$$

where s is the order of multipolarity ($s=1$ for dipole radiation), and the P's are wave functions of the two states involved with energies $E=-1/2\nu^2, E'=-1/2\nu'^2$, respectively. In the CA the latter are replaced by their asymptotic forms, which are purely Coulomb solutions, viz.,

$$P_{\nu l} \sim K W_{\nu, l+1/2}(x), \quad x=2r/\nu \ , \tag{2}$$

and similarly for $P_{\nu' l'}$. Here $W_{\nu\lambda}$ denotes a Whittaker function,[17] which vanishes exponentially when $x\to\infty$, but is irregular at the origin for noninteger ν. For the normalization constant K we use Hartree's generalized hydrogenic form

$$K=[\nu^2\Gamma(\nu-l)\Gamma(\nu+l+1)]^{-1/2} \ . \tag{3}$$

A more refined normalization is required only for low values of ν, especially when $\nu < l+1$.[3,18] The Whittaker function in Eq. (2) is given simply, although with only limited accuracy, by its truncated asymptotic expansion

$$W_{\nu,l+1/2}(x)\sim e^{-x/2}x^{\nu}\sum_{q=0}^{N}b_q x^{-q}\ ,$$
$$b_q=(-1)^q(-\nu+l+1)_q(-\nu-l)_q/q!\ , \tag{4}$$

where

$$(a)_q=a(a+1)\cdots(a+q-1)=\Gamma(a+q)/\Gamma(a)\ ,$$
$$(a)_0=1\ , \tag{5}$$

is the so-called Pochhammer symbol.[19] From its definition it readily follows that

$$(a)_q=(-1)^q(1-a-q)_q=(-1)^q\Gamma(1-a)/\Gamma(1-a-q)\ . \tag{6}$$

Using this property the sum in Eq. (4) is easily reversed to yield

$$\sum_{q=0}^{N}b_q x^{-q}=b_N x^{-N}\sum_{q=0}^{N}d_q x^q\ ,$$
$$d_q=(-N)_q/(\nu-l-N)_q(\nu+l+1-N)_q\ . \tag{7}$$

It is instructive to relate the preceding formulas with the theory of generalized hypergeometric functions.[20,21] Thus the sum in Eq. (4) is indeed a truncation of the series

$${}_2F_0(-\nu+l+1,-\nu-l;-1/x)\ , \tag{8}$$

while the sum in the right-hand side of Eq. (7) represents exactly the function

$${}_2F_2(-N,1;\nu-l-N,\nu+l+1-N;x)\ . \tag{9}$$

If ν is an integer, say, $\nu=n>l+1$, then the sum in Eq. (4) terminates naturally after $N=n-l-1$ terms, and Eq. (9) reduces to

$${}_1F_1(-n+l+1;2l+2;x)\ , \tag{10}$$

which is essentially an associated Laguerre polynomial, so that we retrieve the familiar hydrogenic wave function.

Since the series ${}_2F_0$ has zero radius of convergence, it is clear that increasing N will eventually deteriorate, rather than improve, the accuracy. However, using the truncated asymptotic expansion in Eq. (4) with N close to $\nu-l-1$ presents a twofold advantage, since it provides a reasonable approximation to $W_{\nu,l+1/2}$ in the region which gives the major contribution to the RI, and at the same time it simulates the behavior of the true wave function $P_{\nu l}$ at short range.

We now substitute Eq. (4) for $P_{\nu l}$, and the reversed sum of Eq. (7) for $P_{\nu' l'}$ into Eq. (1). Term by term integration gives

$$R_s=KK'b_{N'}\sum_{q=0}^{N}b_q(2/\nu)^{\nu-q}$$
$$\times\sum_{q'=0}^{N'}d_{q'}(2/\nu')^{\nu'-N'+q'}(\nu\nu'/\nu+\nu')^{\rho}\Gamma(\rho)$$
$$(\rho=\nu+\nu'-N'-q+q'+s+1)\ . \tag{11}$$

In the special case when ν' equals an integer n' the sum over q' terminates for $N'=n'-l'-1$, so that in Eq. (11) one has

$$d_{q'}=(-N')_{q'}/(q')!(2l'+2)_{q'}\ ,$$
$$\Gamma(\rho)=\Gamma(\sigma+q')=(\sigma)_{q'}\Gamma(\sigma)\ , \tag{12}$$
$$\sigma=\nu+l'+s+2-q\ ,$$

and the expression of the RI becomes

$$R_s=KK'b_{N'}(2/\nu)^{\nu}(2/n')^{l'+1}$$
$$\times\sum_{q}b_q(\nu/2)^q(\nu n'/\nu+n')^{\sigma}\Gamma(\sigma)$$
$$\times\sum_{q'}d_{q'}(\sigma)_{q'}(2\nu/\nu+n')^{q'}\ . \tag{13}$$

Equation (13) is clearly equivalent to the Bates-Damgaard double summation, but in the new form the last sum is readily seen to represent the polynomial

$${}_2F_1(-N',\sigma;2l'+2;2\nu/\nu+n')\ , \tag{14}$$

and we recover the result of van Regemorter and coworkers.[12,13] This is extremely useful since it allows us to generate the corresponding sums recursively as a whole by using contiguity relations for the Gauss hypergeometric functions, thus avoiding dramatic cancellations between their terms when n' is very large.

In order to achieve a continuous interpolation for noninteger values of ν' we shall simply go back to Eq. (11) and make for N' (which plays the role of a fictitious radial quantum number) the natural choice $N'=\langle\nu'\rangle-l'-1$. Here $\langle\cdots\rangle$ denotes the nearest integer, related to the more familiar integer part $[\cdots]$ by $\langle\nu'\rangle=[\nu'+\frac{1}{2}]$. Putting

$$\delta'=\nu'-\langle\nu'\rangle,\quad -0.5\le\delta'<0.5 \tag{15}$$

and proceeding as above one finds

$$R_s=KK'b_{N'}(2/\nu)^{\nu}(2/\nu')^{l'+1+\delta'}$$
$$\times\sum_{q}b_q(\nu/2)^q(\nu\nu'/\nu+\nu')^{\sigma}\Gamma(\sigma)$$
$$\times\sum_{q'}d_{q'}(\sigma)_{q'}(2\nu/\nu+\nu')^{q'}\ , \tag{16}$$

with

$$d_{q'}=(-N')_{q'}/(1+\delta')_{q'}(2l'+2+\delta')_{q'}\ ,$$
$$\sigma=\nu+l'+\delta'+s+2-q\ . \tag{17}$$

The sum over q' can be identified as a generalized hypergeometric polynomial[20,21]

$${}_3F_2(-N',1,\sigma;1+\delta',2l'+2+\delta';2\nu/\nu+\nu')\ , \tag{18}$$

and for $\delta'=0$ the latter obviously reduces to that of Eq. (14). Although the new polynomials look a little bit more complicated, it is again possible to compute them very accurately by using recurrence relations. This, of course, is the most important point. The necessary formulas do not seem to be available in standard tables, but they can be worked out from a canonical set of contiguity relations for ${}_pF_q$ functions given by Rainville.[21] We show in the Appendix that the following inhomogeneous three-term recurrence relation holds:

$$\begin{aligned}(b+n)(c+n)f_{n+1} &= (n+1)[b+c-a-1+n+(a+n)(1-x)]f_n \\ &\quad -n(n+1)(1-x)f_{n-1}+(1-b)(1-c)\ , \qquad (19)\end{aligned}$$

where

$$f_n(x)={}_3F_2(-n,1,a;b,c;x)\ . \qquad (20)$$

If $b=1$ or $c=1$ one recovers the recurrence relation for ${}_2F_1$ used by van Regemorter and co-workers.[12,13] To start the recurrence it suffices to consider

$$f_0=1,\quad f_1=1-ax/bc\ . \qquad (21)$$

Since a_1 a_2, and a_3 enter in a symmetrical way, one can of course apply Eq. (A12) by taking $a_1=a$, $a_2=1$, $a_3=-n$. In this way it is possible to generate the values of all the required polynomials from just two of them (e.g., for $q=0,1$), exactly as in the case of integer ν'.

Taking into account Eqs. (4), (17), and (18), we arrive at the following explicit expression for the RI in Eq. (16):

$$\begin{aligned}R_s &= (-1)^{N'}[\Gamma(\nu'+l'+1)\Gamma(\nu'-l')/\Gamma(\nu+l+1)\Gamma(\nu-l)]^{1/2}(\nu\nu')^{-1} \\ &\quad\times\{\Gamma(\nu+l'+\delta'+s+2)/[(N')!\Gamma(1+\delta')\Gamma(2l'+2+\delta')]\}(2/\nu)^{\nu}(2/\nu')^{l'+1+\delta'}(\nu\nu'/\nu+\nu')^{\nu+l'+\delta'+s+2} \\ &\quad\times\sum_q c_q\,{}_3F_2(-N',1,\nu+l'+\delta'+s+2-q;1+\delta',2l'+2+\delta';2\nu/\nu+\nu')\ , \qquad (22)\end{aligned}$$

where the coefficients c_q satisfy the recurrence relation

$$c_q=\frac{l(l+1)-(\nu-q)(\nu-q+1)}{q(\nu+l'+\delta'+s+2-q)}\left[\frac{\nu+\nu'}{2\nu'}\right]c_{q-1} \qquad (q\geq 1)\ , \qquad (23)$$

with $c_0=1$. This result, which is indeed equivalent to the one derived in Ref. 14, reduces for $\delta'=0$ to the formula of Hoang-Binh *et al.*[13]

Until now nothing has been assumed about the ordering of the two levels, and we have no definite rule for truncating the sum in Eq. (22). As a matter of fact we are faced here with an ambiguity already present in the Bates-Damgaard double-summation formula. However, a quick glance at Eq. (23) shows that if ν' is the larger of the two effective quantum numbers then the remaining sum possesses the quite unexpected property of being convergent, which of course settles the problem in the most remarkable way (in this respect it should be noticed that for large q the hypergeometric polynomials behave like $q^{N'}$). The asymptotic character of the expansion is, however, still present in the fact that sums based on polynomials of different degrees yield in general different limits. In order to get consistency with the Bates-Damgaard procedure it might indeed be necessary to use polynomials of higher degree. Formally this amounts to replacing N' by $N'+k'$ and δ' by $\delta'-k'$ in Eqs. (22) and (23). This will be illustrated by numerical examples in Sec. V.

III. MODIFIED COULOMB APPROXIMATION

In this section we describe a quite different approach, closely related to the procedure used by Hylleraas[1] to evaluate analytically the RI associated with $\nu s-n'p$ transitions (more especially for $n'=2,3,4$). Thus instead of using asymptotic series for both Whittaker functions we shall treat one of them exactly by means of a contour-integral representation. The standard form of the latter is[17]

$$\begin{aligned}W_{\nu,l+1/2}(x) &= (i/2\pi)\Gamma(\nu-l)e^{-x/2}x^{\nu} \\ &\quad\times\int_{\infty}^{(0+)}dt\,e^{-t}(-t)^{l-\nu}(1+t/x)^{l+\nu}\ , \qquad (24)\end{aligned}$$

where the integration path starts at infinity on the real axis, encircles the origin counterclockwise, and goes back to infinity. A more convenient form for the present calculation is obtained by the change of variable $t\rightarrow xt/(1-t)$

$$\begin{aligned}W_{\nu,l+1/2}(x) &= (i/2\pi)\Gamma(\nu-l)x^{l+1} \\ &\quad\times\int_{1}^{(0+)}dt\,e^{-(x/2)(1+t)/(1-t)} \\ &\quad\times(-t)^{l-\nu}(1-t)^{-2l-2}\ . \qquad (25)\end{aligned}$$

In both integrals a cut is assumed along the positive real axis $t>0$ $[|\arg(-t)|<\pi]$. Notice that for $l=0$ (s states) Eq. (25) can be transformed further by partial integration into

$$\begin{aligned}W_{\nu,1/2}(x) &= (i/2\pi)\Gamma(\nu+1) \\ &\quad\times\int_{1}^{(0+)}dt\,e^{-(x/2)(1+t)/(1-t)}(-t)^{-1-\nu}\ , \qquad (26)\end{aligned}$$

from which one readily finds $W_{\nu,1/2}(0)=\Gamma(\nu)\sin(\pi\nu)/\pi$. As a matter of fact, Hylleraas used contour integrals for both states, which was possible because for $l'=1$ he restricted to hydrogenic quantum numbers $\nu'=n'$ (regular solution). The convergence of the RI then raises no problem at all since, as we have just seen, the s-state Whittaker function is finite at the origin for any ν. Of course, the normalization integral for the latter also converges, and Hylleraas was able to evaluate it in closed form. His result reads

$$\int_0^{\infty} dr\, W^2_{\nu,1/2}(2r/\nu) = \nu\Gamma^2(\nu+1)\left[1-[\psi'(\nu)-1/\nu-1/2\nu^2]\frac{\sin^2\pi\nu}{\pi^2}\right], \tag{27}$$

where ψ is the logarithmic derivative of the Γ function.[19] The second term in the large square brackets, which vanishes for $\nu=n$ and for $\nu\rightarrow\infty$, measures the deviation from the hydrogenic normalization in Eq. (3).

Turning back to the general case, we now use Eq. (25) for $P_{\nu' l'}$ and again Eq. (4) for $P_{\nu l}$. This will ensure in general the required insensitiveness of the RI to the singular short-range behavior of the first Whittaker function ($W_{\nu',l'+1/2}\simeq x^{-l'}$). Once these substitutions have been made, the integration over r is easily performed and we get

$$R_s=(i/2\pi)\Gamma(\nu'-l')KK'(2/\nu)^{\nu}(2/\nu')^{l'+1}\sum_q b_q(\nu/2)^q(\nu\nu'/\nu+\nu')^{\sigma}\Gamma(\sigma)\int_1^{(0+)}dt(-t)^{l'-\nu'}(1-t)^{\nu-l'+s-q}(1-xt)^{-\sigma}\ , \tag{28}$$

where $x=(\nu'-\nu)/(\nu'+\nu)$, and σ is defined as in Eq. (12). The remaining contour integral is readily expressed in terms of a Gauss hypergeometric function. One has indeed[20,22]

$$ {}_2F_1(a,b;c;x)=(i/2\pi)[\Gamma(c)\Gamma(1-a)/\Gamma(c-a)]\int_1^{(0+)}dt(-t)^{a-1}(1-t)^{c-a-1}(1-xt)^{-b}\ , \qquad \mathrm{Re}(c-a)>0,\quad a\neq 1,2,\ldots \tag{29}$$

so that the final form of Eq. (28) reads

$$R_s=KK'(2/\nu)^{\nu}(2/\nu')^{l'+1}(\nu\nu'/\nu+\nu')^{\nu+l'+s+2}[\Gamma(\nu-l'+s+1)\Gamma(\nu+l'+s+2)/\Gamma(\nu-\nu'+s+2)]$$
$$\times\sum_q a_q\, {}_2F_1(-\nu'+l'+1,\nu+l'+s+2-q;\nu-\nu'+s+2-q;x)\ . \tag{30}$$

with $a_0=1$, and for $q\geq 1$

$$a_q=\frac{\nu'-\nu-s-2+q}{q}\,\frac{l(l+1)-(\nu-q)(\nu-q+1)}{l'(l'+1)-(\nu-q+s+1)(\nu-q+s+2)}\left[\frac{\nu+\nu'}{2\nu'}\right]a_{q-1}\ . \tag{31}$$

A standard transformation of ${}_2F_1$ leads to the useful alternative form

$$R_s=KK'(2/\nu)^{\nu}(2/\nu')^{\nu'}(\nu\nu'/\nu+\nu')^{\nu+\nu'+s+1}[\Gamma(\nu-l'+s+1)\Gamma(\nu+l'+s+2)/\Gamma(\nu-\nu'+s+2)]$$
$$\times\sum_q a_q\, {}_2F_1(-\nu'+l'+1,-\nu'-l';\nu-\nu'+s+2-q;y)\ , \tag{32}$$

where $y=x/(x-1)=(\nu-\nu')/2\nu$. Of course, the validity of this form is restricted to the case when $|y|<1$.

It is instructive to discuss in some detail the special case $\nu'=\nu$. The argument x then vanishes and we have ${}_2F_1=1$ in all terms. Moreover, from Eq. (31) one has $a_q=0$ for $q\geq s+2$, so that the sum in Eq. (30) actually contains just a few terms. The resulting formula may be written as

$$\langle \nu l|r^s|\nu l'\rangle=(-\nu/2)^{s-1}[\Gamma(\nu+l+1)\Gamma(\nu-l)/\Gamma(\nu+l'+1)\Gamma(\nu-l')]^{1/2}$$
$$\times\frac{(l'-l+s+1)!(l-l'+s+1)!}{4(s+1)!}\sum_{q=0}^{s+1}(-1)^q\left[\begin{matrix}s+1\\ q\end{matrix}\right]\left[\begin{matrix}\nu+l'+q\\ l'-l+s+1\end{matrix}\right]\left[\begin{matrix}\nu-l'-1+q\\ l-l'+s+1\end{matrix}\right], \tag{33}$$

where $\binom{\alpha}{\beta}$ are binomial coefficients.[19] This is the generalization to noninteger ν of a formula first derived by Schrödinger in the hydrogenic case $\nu=n$,[23] and rediscovered several times afterwards.[4] If, in addition, we let $l'=l$, Eq. (33) simplifies further and provides a general formula for the expectation value of r^s,

$$\langle \nu l|r^s|\nu l\rangle=\tfrac{1}{4}(-\nu/2)^{s-1}(s+1)! \times \sum_{q=0}^{s+1}(-1)^q\binom{s+1}{q}\binom{\nu+l+q}{s+1} \times \binom{\nu-l-1+q}{s+1} . \tag{34}$$

In particular it is easily verified that for $s=0$ Eq. (34) reduces to $\langle \nu l|\nu l\rangle=1$, which means that with the new mixed procedure the approximate wave functions of the CA are exactly normalized. For $s=1$ and $l'=l-1$ (dipole transitions) Eq. (33) gives

$$\langle \nu l|r|\nu l-1\rangle=(3\nu/2)(\nu^2-l^2)^{1/2} . \tag{35}$$

Similarly, for $s=2$ (quadrupole transitions) one finds

$$\langle \nu l|r^2|\nu l-2\rangle=(5\nu^2/2)\{(\nu^2-l^2)[\nu^2-(l-1)^2]\}^{1/2} , \tag{36}$$

$$\langle \nu l|r^2|\nu l\rangle=(\nu^2/2)[5\nu^2+1-3l(l+1)] . \tag{37}$$

Finally, for $s=-1$ one has

$$\langle \nu l|r^{-1}|\nu l-1\rangle=\nu^{-2}[(\nu-l)/(\nu+l)]^{1/2} , \tag{38}$$

a matrix element of interest for bremsstrahlung calculations. The results for the expectation values have been obtained previously by Szabo and Adelman.[24] To summarize, Eq. (33) shows that in the framework of the CA, when $\nu'\rightarrow\nu$ any matrix element tends towards the corresponding hydrogenic result with n replaced by the noninteger effective principal quantum number ν.

The numerical evaluation of the RI from Eqs. (30) and (32) can be done quickly to the desired accuracy, especially when ν' is taken to be the larger of the two effective quantum numbers, for this again ensures convergence of the sum [of course, if one of the states is hydrogenic, one might prefer to set ν equal to the principal quantum number n of that state, irrespective to ν', since Eq. (30) then gives exactly a finite sum]. Although, in general, the hypergeometric functions here do not reduce to polynomials, that is no real impediment, since the modulus of x is always less than unity, and even becomes very small when both ν and ν' are large compared to their difference. The Gauss series then converge so rapidly that no cancellation problem arises. Their values can therefore be computed directly, without resorting to contiguity relations. Notice that when x is small y is of the same order, and therefore it does not matter very much which formula is used. Sample numerical calculations will be presented in Sec. V.

IV. ORBITAL QUANTUM DEFECT

As mentioned before, the truncated asymptotic expansion in Eq. (4) with N close to $\nu-l-1$ provides indeed a simple approximate wave function behaving almost correctly also when $r\rightarrow 0$. An alternative way of achieving a similar result is the so-called orbital quantum defect (OQD) method, first introduced by Simons,[15] and developed further by Gruzdev and Sherstyuk.[16] That this method is an appealing one, though not popular enough among physicists, is testified by a recent paper[25] which presents almost identical ideas, without any reference to Simons's work.

In the OQD method the true atomic wave function is approximated by

$$P_{\nu l}\simeq K W_{\nu,\lambda+1/2}(2r/\nu) , \quad K=[\nu^2\Gamma(\nu-\lambda)\Gamma(\nu+\lambda+1)]^{-1/2} , \tag{39}$$

where λ is a real number close to l such that $\nu-\lambda$ equals a positive integer. It is readily seen that changing l into λ in Eq. (4) will indeed stop the summation after a finite number of terms, yielding the exact expression

$$W_{\nu,\lambda+1/2}(x)=e^{-x/2}x^{\nu}\sum_{q=0}^{N}b_q x^{-q} , \quad b_q=(-1)^q(-N)_q(-\nu-\lambda)_q/q! , \tag{40}$$

with $N=\nu-\lambda-1$ (according to our assumption N is a nonnegative integer). On account of Eqs. (7) and (10) this may be rewritten as

$$W_{\nu,\lambda+1/2}(x)=b_N e^{-x/2}x^{\lambda+1}{}_1F_1(-N;2\lambda+2;x) , \quad b_N=(-1)^N\Gamma(\nu+\lambda+1)/\Gamma(2\lambda+2) , \tag{41}$$

which makes apparent the similarity with the hydrogenic case (N plays the role of the radial quantum number, equal to the number of nodes). The new approximation defined in Eq. (39) is obviously regular at the origin, and it will be shown below that the normalization integral is exactly equal to 1. In principle, the best choice for λ, which induces minimal alterations in the long-range behavior of the wave function (location of distant nodes, asymptotic amplitude) is

$$\lambda=l+\delta, \quad \delta=\nu-\langle\nu\rangle , \tag{42}$$

giving $N=\langle\nu\rangle-l-1$. This value is fine for Rydberg states, but for low-lying levels a different prescription may sometimes give better results (see Sec. V).

It is worth mentioning that the integral representations Eqs. (24) and (25), are still valid when l is replaced by λ. However, since the difference $\nu-\lambda$ is an integer, the point $t=0$ is no longer a branch point of the integrand. Starting and ending the integration along the real axis then gives two canceling contributions, so that the contours can be effectively reduced to small circles around the origin. For instance, instead of Eq. (24) we have now

$$W_{\nu,\lambda+1/2}(x)=(i/2\pi)N!e^{-x/2}x^{\nu} \times \int^{(0+)}dt\, e^{-t}(-t)^{-N-1}(1+t/x)^{-2\lambda-2} \quad (\nu-\lambda=N+1) , \tag{43}$$

and the theorem of residues can be applied to derive the explicit expressions given above. Similarly, Eq. (25) becomes

$$W_{\nu,\lambda+1/2}(x)=(i/2\pi)N!x^{\lambda+1}\times\int^{(0+)}dt\,e^{-(x/2)(1+t)/(1-t)}\times(-t)^{-N-1}(1-t)^{-2\lambda-2}\quad(\nu-\lambda=N+1)\ , \tag{44}$$

where again the point $t=0$ is a pole of order $N+1$.

Equation (39) is usually interpreted by referring to a model atomic potential of the form $-1/r+c/r^2$ [the Whittaker function in the right-hand side (RHS) is indeed an eigenfunction of such a potential, considered by Fues[26] in the early days of quantum mechanics]. An alternative and perhaps more appropriate interpretation is in terms of Regge states for the Coulomb potential.[27] These are regular solutions of the Schrödinger equation that realize a smooth interpolation between states of different angular momenta when the energy is allowed to vary continuously (Regge trajectory). It is clear that the RHS of Eq. (39) is precisely a Regge state corresponding to the energy $-1/2\nu^2$.

In the OQD approximation the multipole RI of Eq. (1) reads

$$R_s=KK'\int_0^\infty dr\,W_{\nu,\lambda+1/2}(2r/\nu)r^sW_{\nu',\lambda'+1/2}(2r/\nu')\ . \tag{45}$$

Inserting Eq. (41) for both states one immediately obtains

$$R_s=\tilde{K}\tilde{K}'\sum_{q=0}^{N}\sum_{q'=0}^{N'}\frac{(-N)_q(-N')_{q'}\Gamma(\alpha)}{(2\lambda+2)_q(2\lambda'+2)_{q'}(q)!(q')!}\times\left[\frac{2}{\nu}\right]^q\left[\frac{2}{\nu'}\right]^{q'}\left[\frac{\nu\nu'}{\nu+\nu'}\right]^\alpha\quad(\alpha=\lambda+\lambda'+q+q'+s+3)\ , \tag{46}$$

where

$$\tilde{K}=(-1)^N\frac{(2/\nu)^{\lambda+1}}{\nu\Gamma(2\lambda+2)}\left[\frac{\Gamma(\nu+\lambda+1)}{\Gamma(\nu-\lambda)}\right]^{1/2},\quad N=\nu-\lambda-1 \tag{47}$$

and similarly for $\tilde{K}'$. The double sum above can be expressed in terms of an Appell hypergeometric series (here a polynomial) of two variables, viz.,

$$R_s=\tilde{K}\tilde{K}'(\nu\nu'/\nu+\nu')^{\lambda+\lambda'+s+3}\Gamma(\lambda+\lambda'+s+3)\times F_2(\lambda+\lambda'+s+3;-N,-N';2\lambda+2,2\lambda'+2;z,z')\ , \tag{48}$$

where $z=2\nu'/(\nu+\nu')$, $z'=2\nu/(\nu+\nu')$, and F_2 is defined by[20]

$$F_2(a;b,b';c,c';z,z')=\sum_m\sum_n\frac{(a)_{m+n}(b)_m(b')_n}{(c)_m(c')_n m!n!}z^mz'^n\ . \tag{49}$$

When $s=1$ (dipole transitions) Eqs. (48) and (49) reproduce, in a slightly different form, the result already obtained by Simons.[15] However, for highly excited levels we have found that other formulas, which involve a single summation, are more suitable. In the first place, one can simply use the identity $(a)_{m+n}=(a)_m(a+m)_n$ to perform the summation over n and rewrite Eq. (49) as

$$F_2(a;b,b';c,c';z,z')=\sum_m\frac{(a)_m(b)_m}{(c)_m m!}z^m\times{}_2F_1(a+m,b';c';z')\ . \tag{50}$$

The contiguity relations satisfied by ${}_2F_1$ then allow us to considerably improve the computational accuracy, as explained at the end of Sec. II.

An even more efficient expression of the RI is obtained on using Eq. (40) for one state, and the integral representation Eq. (44) for the other. The calculation proceeds exactly as in Sec. III and eventually leads to

$$R_s=KK'(2/\nu)^\nu(2/\nu')^{\lambda'+1}(\nu\nu'/\nu+\nu')^{\nu+\lambda'+s+2}[\Gamma(\nu-\lambda'+s+1)\Gamma(\nu+\lambda'+s+2)/\Gamma(\nu-\nu'+s+2)]\times\sum_{q=0}^{N}a_q\,{}_2F_1(-N',\nu+\lambda'+s+2-q;\nu-\nu'+s+2-q;x)\ , \tag{51}$$

with $x=(\nu'-\nu)/(\nu'+\nu)$. The coefficients a_q satisfy Eq. (31) with l,l', replaced by λ,λ', respectively (it is easily seen that $a_q=0$ for $q\geq N+1$). Needless to say, the direct term by term evaluation of the hypergeometric polynomials in Eq. (51) when ν and ν' are large presents no special difficulty.

For $s=0$, $\nu=\nu'$, and $l=l'$, the sum in Eq. (51) consists of just two terms, and one finds $\langle\nu l|\nu l\rangle=1$. More generally, for the expectation values of r^s Eq. (50) leads to the hydrogenic formulas with ν and λ standing in place of n and l, respectively, e.g.,

$$\langle\nu l|r|\nu l\rangle=\tfrac{1}{2}[3\nu^2-\lambda(\lambda+1)]\ . \tag{52}$$

Although there is no convergence problem in the OQD method, for low-lying levels some questions may arise concerning the best choice of λ, as already mentioned above. In turn, for transitions between highly excited states the method works remarkably well. This point will be discussed further in Sec. V.

V. NUMERICAL RESULTS

In order to test the reliability of the various methods developed above, we have performed numerical calculations for a number of dipole transitions already considered in previous papers.[8,12] To start with, let us dis-

TABLE I. Values of the radial integrals for successive orders of truncation in Eq. (22) starting with $N=\langle \nu \rangle - l - 1$. For each transition the three rows correspond to using polynomials of degree N', $N'+1$, and $N'+2$, respectively ($N'=\langle \nu' \rangle - l' - 1$). Dots indicate that convergence has been achieved.

Transition	N	$N+1$	$N+2$	$N+3$	Ref. 8
7.8*s*-6.2*p*	−7.659	−7.669	−7.669	−7.670	
	−7.668	−7.670	. . .	. . .	−7.670
	−7.668	−7.670	. . .	. . .	
8.4*s*-5.6*p*	3.184	3.127	3.118	3.116	
	3.137	3.135	. . .	. . .	3.135
	3.135	. . .	. . .	. . .	
30.8*s*-29.2*p*	−1.525(2)	. . .	. . .	. . .	
	−1.525(2)	. . .	. . .	. . .	−1.525(2)
	−1.525(2)	. . .	. . .	. . .	
30.8*d*-29.2*f*	+2.111(2)	−1.368(2)	−1.473(2)	−1.481(2)	
	−1.385(2)	−1.477(2)	−1.481(2)	. . .	−1.481(2)
	−1.477(2)	−1.481(2)	. . .	. . .	
31.4*s*-28.6*p*	7.075(1)	7.070(1)	. . .	. . .	
	7.070(1)	. . .	. . .	. . .	7.070(1)
	7.070(1)	. . .	. . .	. . .	
31.4*d*-28.6*f*	1.511(3)	1.351(2)	7.123(1)	6.640(1)	
	8.882(1)	6.718(1)	6.597(1)	6.585(1)	6.584(1)
	6.671(1)	6.590(1)	6.584(1)	. . .	

cuss the convergence of the rearranged Bates-Damgaard expansion introduced in Sec. II (hereafter referred to as method A). The basic approximation here consists in using ${}_3F_2$ polynomials of degree $N'=\langle \nu' \rangle - l' - 1$ and retaining terms up to $q=N=\langle \nu \rangle - l - 1$ in Eq. (22). Further approximations are obtained by extending the summation up to $q=N+k$, and/or using polynomials of higher degree $N'+k'$ (when ν' is not an integer). The effects of such changes are illustrated in Table I for a set of six dipole transitions (here ν' is the larger of the two effective quantum numbers). It may be noticed that, as k increases, the convergence of the sum of *s*-*p* transitions is faster than for *d*-*f* transitions. On the other hand, it should be borne in mind that the expansion is still essentially an asymptotic one, and this explains why the sums over polynomials of different degrees may converge towards different limits (the transition 8.4*s*-5.6*p* offers a striking example). In all the cases the approximation of order $(N+2,N'+2)$ reproduces exactly the value obtained by Picart *et al.*[8] For *s*-*p* transitions, however, the (N,N') approximation also provides a good estimate.

The modified Coulomb approximation described in Sec. III (shortly method B) possesses even better convergence properties. Assuming again $\nu' > \nu$, one usually obtains an accurate estimate of the RI already by truncating the sum in Eqs. (30) or (32) at $q=N=\langle \nu \rangle - l - 1$. The corresponding values for the six transitions considered above are displayed in column B of Table II. Inclusion of terms with $q=N+1,N+2,\ldots$ does not modify the results (to four-digit accuracy). It is remarkable that this method gives practically the same results as the approximation of order $(N+2,N'+2)$ in method A (for convenience, the latter are repeated in column A).

Finally, we applied the OQD approximation (hereafter called method C) to the same transitions using noninteger orbital quantum numbers defined as in Eq. (42). Here the RI is given exactly by a finite double or single summation. The values listed in column C of Table II were obtained with either Eqs. (48)–(50), or Eq. (51). Both formulas are equally suitable even for very excited Rydberg states. However, with the latter the ${}_2F_1$ polynomials can be calculated directly term by term, whereas with the former it is often necessary to resort to recurrence relations. As seen from the table, the OQD estimates have the right order of magnitude, but in some cases may deviate by as much as 15% from those given by methods A and B.

In Table III we show the numerical results obtained for another group of eight dipole transitions between states with much larger effective principal quantum numbers. Clearly, in this case the three new methods all give results in excellent agreement with those of van Regemorter *et al.*[12] The values in column A were computed on using

TABLE II. Comparison of dipole radial integrals obtained by various methods.

	Method		
Transition	A	B	C
7.8*s*-6.2*p*	−7.670	−7.670	−7.434
8.4*s*-5.6*p*	3.135	3.135	3.559
30.8*s*-29.2*p*	−1.525(2)	−1.525(2)	−1.518(2)
30.8*d*-29.2*f*	−1.481(2)	−1.481(2)	−1.456(2)
31.4*s*-28.6*p*	7.070(1)	7.070(1)	7.251(1)
31.4*d*-28.6*f*	6.584(1)	6.583(1)	7.134(1)

TABLE III. Estimates of radial integrals for dipole transitions between very high Rydberg states.

Transition	Method *A*	*B*	*C*	Ref. 12
$39.8s$-$40p$	2.288(3)	2.288(3)	2.289(3)	2.288(3)
$39.5s$-$40p$	1.767(3)	1.767(3)	1.769(3)	1.767(3)
$38.5s$-$40p$	−2.214(2)	−2.214(2)	−2.212(2)	−2.214(2)
$37.5s$-$40p$	8.623(1)	8.623(1)	8.606(1)	8.621(1)
$99.8s$-$100p$	1.431(4)	1.431(4)	1.431(4)	1.431(4)
$99.5s$-$100p$	1.106(4)	1.106(4)	1.106(4)	1.105(4)
$98.5s$-$100p$	−1.421(3)	−1.421(3)	−1.421(3)	−1.421(3)
$97.5s$-$100p$	5.664(2)	5.664(2)	5.660(2)	5.665(2)

the approximation of order (N,N'). As a matter of fact, since here the upper level is hydrogenic (ν' integer), this calculation simply duplicates the one of Ref. 12. However, the numbers in columns B and C were produced by entirely different formulas.

For completeness we provide in Table IV matrix elements for a few s-d and p-p quadrupole transitions. Here the entries in the last column were calculated from semiclassical formulas derived recently.[11] For the latter the parameters were chosen according to the analysis of Oumarou *et al.*,[28] and the relevant Anger functions were evaluated from their rapidly convergent series expansions.[29,30] It appears on inspection that methods A and B give again identical results. For s-d transitions method C errs by only a few percent, but for the $7.8p$-$6.2p$ transition the deviation attains about 20%. On the other hand, the semiclassical estimates are in very good agreement with those of columns A and B, and become increasingly better as we go to higher levels.

VI. CONCLUSIONS

In the present work we have devised three different methods for applying the Coulomb approximation in a computationally effective way to radiative multipole transitions between very high Rydberg states. A common feature of these methods is that the radial integrals are expressed as simple sums over some hypergeometric functions (usually polynomials). This opens the possibility of using certain recurrence relations satisfied by the latter in order to avoid, when necessary, loss of accuracy due to huge cancellations among their individual terms. On the other side, the radial integrals of interest are now calculated directly as they stand, and no additional interpolation or extrapolation is required. It is hoped that the new methods will be found useful in future calculations.

ACKNOWLEDGMENTS

The author is grateful to A. R. Edmonds, H. van Regemorter, N. Tran-Minh, and D. Hoang-Binh for helpful conversations. The Division de Physique Théorique is "Laboratoire associé au Centre National de la Recherche Scientifique."

APPENDIX

We sketch here the derivation of the recurrence relation satisfied by the polynomials

$$f_n(x)={}_3F_2(-n,1,a;b,c;x)\ , \qquad \text{(A1)}$$

where ${}_3F_2$ is a generalized hypergeometric series defined by

$${}_3F_2(a_1a_2a_3;b_1b_2;x)=\sum_{m=0}^{\infty}\frac{(a_1)_m(a_2)_m(a_3)_m}{(b_1)_m(b_2)_m m!}x^m \qquad \text{(A2)}$$

(for arbitrary parameters this series always converges when $|x|<1$).

Rainville,[21] who considered the general case of hypergeometric series ${}_pF_q$ with p parameters of type a and q parameters of type b, obtained a canonical set of $(2p+q)$ linearly independent contiguity relations. When $p=q+1$ these read

TABLE IV. Radial integrals for quadrupole transitions.

Transition	Method *A*	*B*	*C*	WKB
$7.8s$-$6.2d$	−2.049(2)	−2.049(2)	−2.084(2)	−2.066(2)
$7.8p$-$6.2p$	−1.270(2)	−1.270(2)	−1.520(2)	−1.229(2)
$30.8s$-$29.2d$	−5.825(4)	−5.825(4)	−5.998(4)	−5.825(4)
$30.8p$-$29.2p$	−4.816(4)	−4.816(4)	−5.038(4)	−4.808(4)
$31.4s$-$28.6d$	4.314(4)	4.314(4)	4.302(4)	4.310(4)
$31.4p$-$28.6p$	4.256(4)	4.256(4)	4.204(4)	4.247(4)
$40.8s$-$39.2d$	−1.773(5)	−1.773(5)	−1.817(5)	−1.773(5)
$40.8p$-$39.2p$	−1.527(5)	−1.527(5)	−1.579(5)	−1.525(5)

$$(a_1-a_k)F=a_1F(a_1+1)-a_kF(a_k+1)\ , \tag{A3}$$

$$(a_1-b_k+1)F=a_1F(a_1+1)-(b_k-1)F(b_k-1)\ , \tag{A4}$$

$$(1-x)F=F(a_k-1)+x\sum_{i=1}^{q}W_{ki}F(b_i+1)\ , \tag{A5}$$

$$[(1-x)a_1+(A-B)x]F=(1-x)a_1F(a_1+1)-x\sum_{i=1}^{q}U_iF(b_i+1)\ , \tag{A6}$$

where $F={}_pF_q(a_1,\ldots,a_p;b_1,\ldots,b_q;x)$, $A=\sum_i a_i$, $B=\sum_i b_i$,

$$U_i=\prod_s(a_s-b_i)\Big/\left[b_i\prod_{s\neq i}(b_s-b_i)\right]\ ,$$

$$W_{ki}=U_i/(a_k-b_i)\quad(i=1,\ldots,q;\ k=1,\ldots,p) \tag{A7}$$

and the notation $F(a\pm1),F(b\pm1)$, is meant to emphasize the unique parameter incremented by ±1.

In our problem $p=3$ and $q=2$. Solving Eqs. (A5) with $k=1$ and $k=2$ for $F(b_1+1)$ and $F(b_2+1)$ we find

$$x(a_1-a_2)(a_3-b_1)F(b_1+1)=b_1(a_1-b_2)Q_1-b_1(a_2-b_2)Q_2\ , \tag{A8}$$

$$x(a_1-a_2)(a_3-b_2)F(b_2+1)=b_2(a_1-b_1)Q_1-b_2(a_2-b_1)Q_2\ , \tag{A9}$$

where we set for brevity

$$Q_k=(1-x)F-F(a_k-1),\quad k=1,2\ . \tag{A10}$$

Substitution into the sum appearing in the RHS of Eq. (A6) gives after simple algebra

$$\begin{aligned}(a_1-a_2)[(A-B)x+a_1(1-x)]F&=(a_1-a_2)(1-x)a_1F(a_1+1)\\&\quad-(a_1-b_1)(a_1-b_2)Q_1+(a_2-b_1)(a_2-b_2)Q_2\ .\end{aligned} \tag{A11}$$

Taking into account Eq. (A10) and regrouping the terms one finally has

$$\begin{aligned}(a_1-a_2)[(A-B)+(a_1-a_3)(1-x)]F&=a_1(a_1-a_2)(1-x)F(a_1+1)\\&\quad+(a_1-b_1)(a_1-b_2)F(a_1-1)\\&\quad-(a_2-b_1)(a_2-b_2)F(a_2-1)\ .\end{aligned} \tag{A12}$$

Now let $a_1=-n$, $a_2=1$, $a_3=a$, $b_1=b$, and $b_2=c$. Then $F(a_2-1)=1$, and Eq. (A12) gives a recurrence relation connecting three successive polynomials f_n, which is precisely Eq. (19) in the main text.

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