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New and rapid method for calculation of electric dipole and quadrupole radial integrals between atomic Rydberg states

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Electric dipole and quadrupole transitions probabilities between two atomic Rydberg states $\nu l, \nu' l'$ have been calculated using three methods. From comparison of results we deduce a new method from which any radial integrals may be obtained very easily using only two functions of the difference $s = \nu - \nu'$. These functions are $g_0(s)$ and $g_1(s)$ which have been calculated in the dipole case [J. Picart, A. R. Edmonds, N. Tran Minh, and R. Pullen, J. Phys. B 11, L651 (1978); A. R. Edmonds, J. Picart, N. Tran Minh, and R. Pullen, J. Phys. B 12, 2781 (1979)].

I. INTRODUCTION

The interpretation of many recent works on high Rydberg states in conventional and laser spectroscopy (for an extensive bibliography see, for example, Fabre[1]), requires the computation of electric multipole transition probabilities for hydrogenic and nonhydrogenic atoms and for a wide range of the parameters $\nu, l; \nu', l'$, in particular for large values of the effective principal quantum numbers ν, ν'.

Electric dipole transitions which account for the overwhelming majority of spectral lines have received much attention. In the hydrogenic cases exact quantum solutions are available,[2,3] and Heisenberg's form of the correspondence principle used by Naccache[4] and Percival and Richards[5] gives close agreement of the semiclassical formula with the exact values. In the nonhydrogenic cases, Bates and Damgaard[6] point out that interpolation applied to certain functions of the radial integrals is a useful procedure. This leads one[7,8] to hope that radial integrals for large ν, ν' might be obtained by a similar extrapolation from values computed for lower ν, ν' using the radial integral method of Edmonds and Kelly[9] which gives exact quantum results for ν and $\nu' \lesssim 35$. We make use of the semiclassical formula[4,5] for the radial integrals to suggest a satisfactory mean of extrapolation. Another method is described by Davydkin and Zon,[10] who use JWKB wave functions and consider the electron as a classical particle moving in accordance with Kepler's law on an ellipse with eccentricity ϵ. They obtain analytic expression for dipole matrix elements by using the quantum-defect method in the quasiclassical approximation (JWKB-QD method). In Sec. II results obtained by the three methods for dipole radial integrals, correspondence principle (CP), our extrapolation method (EXT), and the JWKB-QD method, are recalled. From comparison of results it is shown that radial dipole integrals may be calculated using only the functions $g_0(s)$ and $g_1(s)$ tabulated by Edmonds *et al.*[8] Sections III and IV are devoted to electric quadrupole transitions. Using the same methods as in the dipole case we show that quadrupole matrix elements may be calculated very easily in the two cases allowed by the selection rules. Case $\Delta l = l' - l = 0$ is given in Sec. III and case $\Delta l = \pm 2$ is given in Sec. IV. Section V contains concluding remarks.

We adopt the following conventions in this paper. Atomic units are used. For any electric multipole transitions of L order between ν, l and ν', l' atomic states we set

$$s = \nu - \nu' , \tag{1}$$

$$\Delta l = l' - l . \tag{2}$$

In the hydrogenic case the eccentricity ϵ of the classical Kepler's orbit is defined by

$$\epsilon^2 = \left[1 - \frac{l_c^2}{n_c^2} \right] ; \tag{3}$$

l_c and n_c are mean values of l, l' and n, n', chosen in each case to provide good agreement between exact quantum-mechanical and correspondence results.

To compute radial integrals for large ν, ν' we define, for purposes of extrapolation functions,

$$\phi_L^{\Delta l}(\nu l, \nu' l') = \frac{\langle \nu l \mid r^L \mid \nu' l' \rangle}{\langle \nu_c l \mid r^L \mid \nu_c l' \rangle} , \tag{4}$$

where the denominator is always supposed to be well approximated by the hydrogenic formula. We have $L=1$ and $\Delta l=\pm 1$ for allowed electric dipole transitions, $L=2$ and $\Delta l=0$ (with $l\neq 0$), ± 2 for allowed electric quadrupole transitions.

II. EVALUATION OF RADIAL DIPOLE MATRIX ELEMENTS

A. Hydrogenic case

Naccache[4] has applied Heisenberg's correspondence principle to give the approximation

$$|\langle nl\,|\,r\,|\,n'l'\rangle| = \frac{n_c^2}{2s}\left[\left(1+\Delta l\frac{l_c}{n_c}\right)J_{s+1}(\epsilon s) - \left(1-\Delta l\frac{l_c}{n_c}\right)J_{s-1}(\epsilon s)\right] . \tag{5}$$

He chooses

$$l_c=\frac{l+l'+1}{2} , \tag{6}$$

$$n_c=\frac{2nn'}{n+n'} , \tag{7}$$

and obtains good agreement between exact quantal results and correspondence results.

For purposes of extrapolation we have to consider the function $\phi_1^{\pm 1}$, which, using the definition given in Eq. (4), is

$$\phi_1^{\pm 1}(nl,n'l')=\langle nl\,|\,r\,|\,n'l'\rangle \Big/ 1.5n_c^2\left[1-\frac{l_c^2}{n_c^2}\right]^{1/2} . \tag{8}$$

When $\langle nl\,|\,r\,|\,n'l'\rangle$ is replaced by the above semiclassical formula [Eq. (5)], the MacLaurin series for $\phi_1^{\pm 1}$ in terms of

$$\gamma=\Delta l\frac{l_c}{n_c} , \tag{9}$$

truncated after the term in γ^3, gives a good approximation to $\phi_1^{\pm 1}$. We may write

$$\phi_1^{\pm 1}(nl,n'l')\equiv\phi_1^{\pm 1}(s,\gamma;l_c)=\sum_{p=0}^{3}\gamma^p g_p(s) , \tag{10}$$

the coefficients of γ^p are alternately even and odd functions of s only. We find, for integer values of s,

$$g_0(s)=g_2(s)=\frac{(-1)^s}{3s}[J_{s+1}(s)-J_{s-1}(s)] , \tag{11}$$

$$g_1(s)=\frac{(-1)^s}{3s}[J_{s+1}(s)+J_{s-1}(s)] , \tag{12}$$

$$g_3(s)=\frac{s}{2}g_0(s)+g_1(s) , \tag{13}$$

where $J_{s\pm 1}$ are Bessel's functions.

B. Nonhydrogenic case. Extrapolation method of Picart *et al.* (Ref. 1)

The good results obtained in the hydrogenic case lead us to propose a similar expansion for the nonhydrogenic case. The $g_p(s)$ are obtained by reference of computed values of the radial integrals using the method of Edmonds and Kelly.[9] The functions $g_0(s)\cdots g_3(s)$ are shown in Fig. 1; they have been tabulated[8] for $s=0(0.05)4$. Details are given in Refs. 7 and 8.

C. Nonhydrogenic case. JWKB-QD method of Davydkin and Zon (Ref. 10)

Davydkin and Zon have used a quasiclassical approximation in the quantum-defect method which gives an analytic expression for the dipole matrix element in terms of Anger functions $\mathcal{J}_{s\pm 1}(-\epsilon s)$. The Anger function $\mathcal{J}_\Delta(x)$ is defined by

$$\mathcal{J}_\Delta(x)=\frac{1}{\pi}\int_0^\pi \cos(\Delta\theta-x\sin\theta)d\theta . \tag{14}$$

Properties of Anger functions may be found in Watson,[11] some of them which are used in our calculations are given in Appendix A.

The dipole radial integral can be written[10]

$$\langle \nu l\,|\,r\,|\,\nu'l'\rangle=\frac{\nu_c^2}{s}\left[\left[s(\epsilon-1)\frac{\sin(\pi s)}{\pi s}+\tfrac{1}{2}[\mathcal{J}_{s-1}(-\epsilon s)-\mathcal{J}_{s+1}(-\epsilon s)]-\frac{\gamma}{2}[\mathcal{J}_{s+1}(-\epsilon s)+\mathcal{J}_{s-1}(-\epsilon s)]\right]\right] . \tag{15}$$

Definitions of l_c and γ are the same in the three methods [Davydkin and Zon choose $\nu_c^2=\nu\nu'$; however, numerical results are almost identical with $\nu_c=2\nu\nu'/(\nu+\nu')$]. The functions $\phi_1^{\pm 1}(\nu l,\nu'l')$ deduced from radial integral given in Eq. (15), as in the two methods described above are

$$\phi_1^{\pm 1}(s,\gamma;l_c)=\frac{2}{3\epsilon s}\left[\left[s(\epsilon-1)\frac{\sin(\pi s)}{\pi s}+\tfrac{1}{2}[\mathcal{J}_{s-1}(-\epsilon s)-\mathcal{J}_{s+1}(-\epsilon s)]\right]-\frac{\gamma}{2}[\mathcal{J}_{s+1}(-\epsilon s)+\mathcal{J}_{s-1}(-\epsilon s)]\right] . \tag{16}$$

We find that the MacLaurin series for $\phi_1^{\pm 1}$ in terms of γ, truncated after the term in γ^3, is a good approximation to $\phi_1^{\pm 1}$. The coefficients of γ^p are alternately even and odd functions of s only and may be written in terms of Anger functions. We find for noninteger and integer values of s,

$$g_0(s)=\frac{1}{3s}[\mathcal{J}_{s-1}(-s)-\mathcal{J}_{s+1}(-s)] , \tag{17}$$

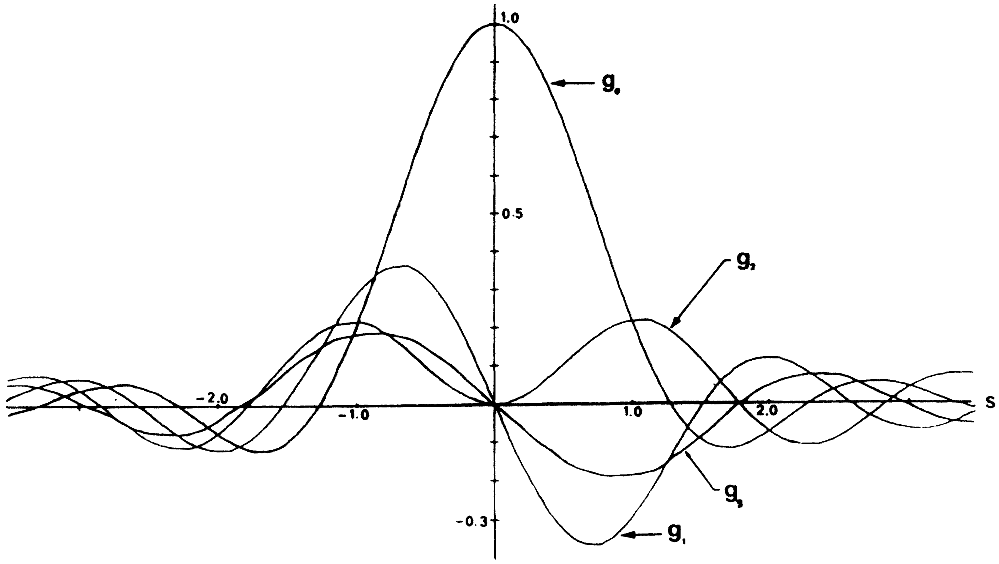

FIG. 1. Graphs of the functions $g_0(s) \cdots g_3(s)$.

$$g_1(s) = -\frac{1}{3s}[\mathcal{J}_{s-1}(-s) + \mathcal{J}_{s+1}(-s)] \,, \tag{18}$$

$$g_2(s) = g_0(s) - \frac{\sin(\pi s)}{\pi s} \,, \tag{19}$$

$$g_3(s) = \frac{s}{2} g_0(s) + g_1(s) \,. \tag{20}$$

Examination of these results shows that in the hydrogenic case, g_i functions derived from Naccache's and from Davydkin and Zon's results are identical. Furthermore, we can see that g_2 and g_3 can be written in terms of g_0 and g_1, therefore dipole radial integrals can be calculated using only g_0 and g_1.

The functions $\phi_1^{\pm 1}$ may be expressed as

$$\begin{aligned} \phi_1^{\pm 1}(\nu l, \nu' l') &= \phi_1^{\pm 1}(s, \gamma; l_c) \\ &= g_0(s) \left[1 + \gamma^2 \left[1 + \frac{s}{2} \right] \right] \\ &\quad + g_1(s)(\gamma + \gamma^3) - \frac{\sin(\pi s)}{\pi s} \gamma^2 \\ &= A g_0(s) + B g_1(s) + C \,. \end{aligned} \tag{21}$$

Coefficients A, B, and C are very easy to compute; the functions $\phi_1^{\pm 1}$ and the radial dipole integral are then obtained very rapidly.

Numerical values of dipole radial integrals obtained using (1) the four functions g_0, g_1, g_2, g_3 tabulated by Edmonds *et al.*,[8] (2) the function $\phi_1^{\pm 1}$ of Eq. (21) expressed in terms of the two functions g_0 and g_1, and (3) the method of Edmonds and Kelly,[9] which gives exact values for ν and $\nu' \lesssim 35$, are given in Table I. We can see that dipole radial integrals may be obtained using only the two functions g_0 and g_1 with almost the same precision than with the four functions.

Using JWKB-QD approximation and the recurrence relations between Anger functions and the derivatives given in Appendix A, we can show that coefficient $g_4(s), \ldots, g_k(s)$ of terms in $\gamma^4, \ldots, \gamma^k$ for all g_k may be expressed as functions of $g_0(s)$ and $g_1(s)$. Functions $g_4, \ldots, g_7$ may be written as

$$g_4(s) = g_0(s) + \frac{s}{4} g_1(s) - \frac{\sin(\pi s)}{\pi s} \,, \tag{22}$$

$$g_5(s) = g_1(s) + \frac{3s}{4} g_0(s) - \frac{\sin(\pi s)}{6\pi} \,, \tag{23}$$

TABLE I. Dipole radial integrals. $\langle \,|r|\, \rangle_{\text{EXT}}$, integrals calculated by the extrapolation method of Picart *et al.*; $\langle \,|r|\, \rangle_{\text{AEXT}}$, integrals calculated by our new approximate method using only the functions $g_0(s)$ and $g_1(s)$; $\langle \,|r|\, \rangle_{\text{EK}}$, integrals calculated by the method of Edmonds and Kelly. The percentage difference is the difference between exact values given by method of Edmonds and Kelly and our new method (AEXT).

Transition	γ	s	$\langle \,\|r\|\, \rangle_{\text{EXT}}$	$\langle \,\|r\|\, \rangle_{\text{AEXT}}$	$\langle \,\|r\|\, \rangle_{\text{EK}}$	Percentage difference
30.8*s*-29.2*p*	0.0334	1.6	−152.46	−152.46	−152.46	0.001
30.8*d*-29.2*f*	0.1001	1.6	−148.09	−148.10	−148.10	0.001
7.6*s*-6.2*p*	0.1447	1.6	−7.6695	−7.6713	−7.6702	0.01
31.4*s*-28.6*p*	0.0334	2.8	70.705	70.707	70.701	0.008
31.4*d*-28.6*f*	0.1002	2.8	65.836	65.853	65.841	0.02
8.4*s*-5.6*p*	0.1488	2.8	3.132	3.131	3.135	0.1

$$g_6(s)=\left[2+\frac{s^2}{6}\right]g_0(s)+\frac{5s}{12}g_1(s)-\frac{\sin(\pi s)}{\pi s}\ , \tag{24}$$

$$g_7(s)=\left[1+\frac{s^2}{24}\right]g_1(s)+\frac{11s}{12}g_0(s)-7\frac{\sin(\pi s)}{24\pi}\ . \tag{25}$$

We can then compute dipole radial integrals even for $\gamma \lesssim 1$. We can set $\gamma_{\max}=0.8$ when the extended series is used.

III. EVALUATION OF QUADRUPOLE RADIAL INTEGRALS BETWEEN STATES WITH $\Delta l = 0$

A. Hydrogenic case

Quantal and semiclassical formulas are identical for $s=0$ if we set

$$l_c^2=l(l+1)-\tfrac{1}{3} \text{ with } l\neq 0\ , \tag{26}$$

which gives

$$\epsilon^2=1-\frac{l(l+1)-\frac{1}{3}}{n_c^2}\ . \tag{27}$$

We choose for n_c the same definition as in the dipole case,

$$n_c=\frac{2nn'}{n+n'}\ .$$

We then have

$$\langle n_c l\,|\,r^2\,|\,n_c l\rangle=2.5n_c^4\left[1-\frac{3}{5}\frac{l_c^2}{n_c^2}\right]\ . \tag{28}$$

We set

$$\gamma^2=\frac{4}{5}\frac{l_c^2}{n_c^2} \tag{29}$$

(the factor $\frac{4}{5}$ is chosen for convenience, as it will be seen below).

For $s\neq 0$, using Heisenberg's form of the correspondence principle we obtain the semiclassical approximation for the quadrupole radial integral,

$$\langle nl\,|\,r^2\,|\,n'l\rangle=(-1)^{s+1}\frac{2n_c^4}{s^2}J_s(\epsilon s)\ , \tag{30}$$

where we use the proper phase factor $(-1)^{s+1}$ to agree, as in the dipole case, with the conventions of Bates and Damgaard[6] and Oertel *et al.*[12] We then have

$$\phi_2^0(nl,n'l)=\phi_2^0(s,\gamma^2;l)=(-1)^{s+1}\frac{4}{5s^2}\frac{J_s(\epsilon s)}{\left[1-\frac{3}{5}\frac{l_c^2}{n_c^2}\right]}\ . \tag{31}$$

The MacLaurin series in terms of γ^2 truncated after the term in γ^2 gives a good approximation to ϕ_2^0:

$$\phi_2^0(s,\gamma^2;l)=\sum_{p=0}^{1}\gamma^{2p}Q_{2p}^{(0)}(s)\ . \tag{32}$$

The coefficients of γ^{2p} are even functions of s only. We find, for integer values of s,

$$Q_0^{(0)}(s)=(-1)^{s+1}\frac{2}{5s^2}[J_{s+1}(s)+J_{s-1}(s)] = -\frac{6}{5s}g_1(s)\ , \tag{33}$$

$$Q_2^{(0)}(s)=(-1)^{s+1}\left[\frac{3}{10s^2}[J_{s+1}(s)+J_{s-1}(s)]+\frac{1}{4s}[J_{s+1}(s)-J_{s-1}(s)]\right] = -\frac{3}{4}\left[\frac{6}{5s}g_1(s)+g_0(s)\right]\ . \tag{34}$$

Values of integrals calculated using the semiclassical formula [Eq. (31)] have been compared with exact quantum-mechanical values to check the validity of our choice of l_c and n_c. The validity of the approximation by series truncated after γ^2 has also been checked numerically. Some examples are given in Table II; in the two cases the precision is very good.

B. Nonhydrogenic case. Extrapolation method

The good results obtained in the hydrogenic case lead us to propose a similar expansion for the nonhydrogenic case. Functions $Q_0^{(0)}(s)$ and $Q_2^{(0)}(s)$ are deduced from values of the quadrupole radial integrals between states

TABLE II. Quadrupole radial integrals $\Delta l=0$ between hydrogenic states. $\langle\,|r^2|\,\rangle_{\mathrm{SC}}$, integrals calculated using the semiclassical formula; $\langle\,|r^2|\,\rangle_{\mathrm{ASC}}$, integrals calculated using the truncated expansion of the approximate semiclassical formula; $\langle\,|r^2|\,\rangle_{\mathrm{EK}}$, exact values of the integrals, calculated by the method of Edmond and Kelly. The percentage difference is the difference between the exact values given by the method of Edmonds and Kelly and the approximate semiclassical formula (ASC).

Transition	γ^2	s	$\langle\,\|r^2\|\,\rangle_{\mathrm{SC}}$	$\langle\,\|r^2\|\,\rangle_{\mathrm{ASC}}$	$\langle\,\|r^2\|\,\rangle_{\mathrm{EK}}$	Percentage difference
8*p*-7*p*	0.0239	1	2703	2705	2706	0.04
10*p*-8*p*	0.0169	2	-1086	-1087	-1093	0.5
31*p*-29*p*	0.0015	2	-1.4209×10^5	-1.4210×10^5	-1.4218×10^5	0.05
31*g*-29*g*	0.0175	2	-1.4023×10^5	-1.4029×10^5	-1.4034×10^5	0.04
26*p*-23*p*	0.0022	3	2.432×10^4	2.432×10^4	2.433×10^4	0.04

with $\Delta l = 0$, computed in the region of ν and ν', where we can use the program of Edmonds and Kelly.[9] The method is similar to that used in the calculations of functions $g_p(s)$.[7,8] The formulas which have been used are given in Appendix B. We have checked the values given by the formula

$$\phi_2^0(\nu l, \nu' l) = \phi_2^0(s, \gamma^2; l) = \sum_{p=0}^{1} \gamma^{2p} Q_{2p}^{(0)}(s) \tag{35}$$

against those obtained from the method of Edmonds and Kelly.[9] We can see from Table III that the error does not exceed 1% for $\nu, \nu' \geq 8$.

C. Nonhydrogenic case. JWKB-QD method

Davydkin and Makarenko[13] use the same approximation as Davydkin and Zon[10] to calculate the radial wave functions. After transformations similar to those used in evaluating dipole matrix elements[10] they obtain quadrupole matrix elements for $\Delta l = 0$, in terms of Anger functions. Obviously, using the same method we obtain the same formula for the quadrupole radial integral, which may be written as

$$\langle \nu l \mid r^2 \mid \nu' l \rangle = \nu_c^4 (1-\epsilon)^2 \frac{\sin(\pi s)}{\pi s} + \epsilon \frac{\nu_c^4}{s^2} [\mathbf{J}_{s+1}(-\epsilon s) + \mathbf{J}_{s-1}(-\epsilon s)] \; . \tag{36}$$

As it was said by Naccache,[4] there are an infinite number of valid choices for l_c and ν_c and to compare results given by the three methods we choose the same definitions of l_c, ν_c, and γ^2 as in the two methods described above.

From Eq. (36) we obtain an analytic expression for the function ϕ_2^0, which is

$$\phi_2^0(\nu l, \nu' l) = \phi_2^0(s, \gamma^2; l) = \frac{2}{5\left[1 - \dfrac{3}{5}\dfrac{l_c^2}{\nu_c^2}\right]} \left[(1-\epsilon)^2 \frac{\sin(\pi s)}{\pi s} + \frac{\epsilon}{s^2} [\mathbf{J}_{s+1}(-\epsilon s) + \mathbf{J}_{s-1}(-\epsilon s)] \right] . \tag{37}$$

The MacLaurin series of ϕ_2^0 in terms of γ^2 gives

$$Q_0^{(0)}(s) = \frac{2}{5s^2} [\mathbf{J}_{s+1}(-s) + \mathbf{J}_{s-1}(-s)] = -\frac{6}{5s} g_1(s) \; , \tag{38}$$

$$Q_2^{(0)}(s) = -\frac{3}{4} \left[\frac{6}{5s} g_1(s) + g_0(s) \right] . \tag{39}$$

These results are identical to results obtained using our extrapolation method.

From Eqs. (38) and (39) we can see that the function ϕ_2^0 and then the quadrupole radial integral may be calculated using only the functions $g_0(s)$ and $g_1(s)$, which are available from the authors for $s = 0(0.05)20$. The function ϕ_2^0 may be approximated by

$$\phi_2^0(s, \gamma^2; l) = D g_1(s) + E g_0(s) \; , \tag{40a}$$

where

$$D = -\frac{6}{5s}(1 + \tfrac{3}{4}\gamma^2) \tag{40b}$$

and

$$E = -\tfrac{3}{4}\gamma^2 \; . \tag{40c}$$

Coefficients D and E are very easy to compute. Values of quadrupole radial integrals obtained using Eqs. (40a)–(40c) are checked against exact values of Edmonds and Kelly[9] in Table III. We can see that quadrupole radial integrals with $\Delta l = 0$ may be calculated as dipole radial integrals using only functions $g_0(s)$ and $g_1(s)$.

From Table III we can see that the errors decrease with s/ν_c, but also with γ^2. However, when s/ν_c is not too large, better precision may be obtained when the expansion of ϕ_2^0 is truncated after the term in γ^4. This is not true for transition 7.9p-6.1p because s is largest here; nevertheless, the error does not exceed 1% even in that case. The coefficient $Q_4^{(0)}(s)$ is also a function of $g_0(s)$

TABLE III. Quadrupole radial integrals $\Delta l = 0$ between nonhydrogenic states. $\langle \mid r^2 \mid \rangle_{\mathrm{EXT}}$, $\langle \mid r^2 \mid \rangle_{\mathrm{AEXT}}$, $\langle \mid r^2 \mid \rangle_{\mathrm{EK}}$, and the percentage difference have the same definition as in Table I.

Transition	γ^2	s	$\langle \mid r^2 \mid \rangle_{\mathrm{EXT}}$	$\langle \mid r^2 \mid \rangle_{\mathrm{AEXT}}$	$\langle \mid r^2 \mid \rangle_{\mathrm{EK}}$	Percentage difference
30.4*p*-29.6*p*	0.0015	0.8	1.0804×10^6	1.0803×10^6	1.0804×10^6	0.01
7.4*p*-6.6*p*	0.0274	0.8	3114.3	3113.8	3.115.5	0.05
30.6*p*-29.4*p*	0.0015	1.2	3.8124×10^5	3.8113×10^5	3.116×10^5	0.008
7.6*p*-6.4*p*	0.0276	1.2	1093.1	1092.8	1092.1	0.06
30.9*p*-29.1*p*	0.0015	1.8	-1.3117×10^5	-1.3107×10^5	-1.3119×10^5	0.09
7.9*p*-6.1*p*	0.0281	1.8	-352.57	-352.32	-357.04	1

and $g_1(s)$ and is given by

$$Q_4^{(0)}(s) = -\frac{3}{8}\left[\frac{9}{5s}g_1(s) + \frac{11}{4}g_0(s) - \frac{5}{4}\frac{\sin(\pi s)}{\pi s}\right] . \qquad (41)$$

IV. EVALUATION OF QUADRUPOLE RADIAL INTEGRALS WITH $\Delta L = \pm 2$

A. Hydrogenic case

For $s = 0$, the quantum-mechanical formula for the radial integral is

$$\langle nl \mid r^2 \mid nl+2 \rangle = \tfrac{5}{2}n^4\left[1 - \frac{(l+1)^2}{n^2}\right]^{1/2} \times \left[1 - \frac{(l+2)^2}{n^2}\right]^{1/2} . \qquad (42)$$

The exact formula is well approximated, with an error term in $O(n^2)$, by

$$\langle nl \mid r^2 \mid nl+2 \rangle = \tfrac{5}{2}n^4\left[1 - \frac{(l+3/2)^2}{n^2}\right] . \qquad (43)$$

The correspondence principle gives the semiclassical formula

$$\langle nl \mid r^2 \mid nl+2 \rangle = \tfrac{5}{2}n^4\epsilon^2 . \qquad (44)$$

The quantal and semiclassical formulas are almost identical if we choose

$$l_c = \frac{l + l' + 1}{2} . \qquad (45)$$

For $s \neq 0$, Heisenberg's correspondence principle gives a semiclassical approximation for the quadrupole radial integral with $\Delta l = \pm 2$, which may be written

$$\langle nl \mid r^2 \mid n'l+\Delta l \rangle = (-1)^{s+1}\frac{2n_c^4}{\epsilon^2 s^2}\{[(2-\epsilon^2)J_s(\epsilon s) - 2\epsilon s(1-\epsilon^2)J_s'(\epsilon s)] + \Delta l(1-\epsilon^2)^{1/2} \times [s(1-\epsilon^2)J_s(\epsilon s) - \epsilon J_s'(\epsilon s)]\} , \qquad (46)$$

where n_c is defined as in the first two cases,

$$n_c = \frac{2nn'}{n+n} . \qquad (47)$$

We set $\gamma = \Delta l l_c / n_c$.

The functions $\phi_2^{\pm 2}(nl,n'l')$ are then given, using Eqs. (4), (43), and (46), by

$$\phi_2^{\pm 2}(nl,n'l') = \phi_2^{\pm 2}(s,\gamma;l_c) = (-1)^{s+1}\frac{4}{5\epsilon^4 s^2}\{[(2-\epsilon^2)J_s(\epsilon s) - 2\epsilon s(1-\epsilon^2)J_s'(\epsilon s)] + \Delta l(1-\epsilon^2)^{1/2}[s(1-\epsilon^2)J_s(\epsilon s) - \epsilon J_s'(\epsilon s)]\} . \qquad (48)$$

We hope that the MacLaurin series for $\phi_2^{\pm 2}$ in terms of γ truncated after the term in γ^3 will give a good approximation to $\phi_2^{\pm 2}$. We then write

$$\phi_2^{\pm 2}(nl,n'l') = \phi_2^{\pm 2}(s,\gamma;l_c) = \sum_{p=0}^{3}\gamma^p Q_p^{(2)}(s) . \qquad (49)$$

Coefficients of γ^p are alternately even and off functions only of s. The even functions $Q_0^2(s)$ and $Q_2^2(s)$ are the same as for transitions with $\Delta l = 0$ (definition of $\gamma^2 = \frac{4}{5}l_c^2/n_c^2$ was used for that reason).

The odd functions may be written

$$Q_1^{(2)}(s) = (-1)^s\frac{2}{5s^2}[J_{s-1}(s) - J_{s+1}(s)] = -\frac{6}{5s}g_0(s) = -\frac{6}{5s}g_2(s) , \qquad (50)$$

$$Q_3^{(2)}(s) = \frac{1}{2}\left[\frac{s}{2}Q_0(s) + Q_1(s)\right] = -\tfrac{1}{2}\left[\tfrac{3}{5}g_1(s) + \frac{6}{5s}g_0(s)\right] . \qquad (51)$$

Values of the quadrupole radial integrals obtained from the semiclassical formula of Eq. (46) and of the expansion given in Eq. (49), using our definitions of l_c, n_c, and γ, are checked against those obtained from the method of Edmonds and Kelly[9] in Table IV. We can see that the quantal and semiclassical results are in good agreement and that the MacLaurin series for $\phi_2^{\pm 2}$ may be truncated after the term in γ^3 for $|\gamma| < 0.4$.

B. Nonhydrogenic case. Extrapolation method

Good results obtained in the hydrogenic case lead us to propose a similar expansion in the nonhydrogenic case.

TABLE IV. Quadrupole radial integrals $|\Delta l|=2$ between hydrogenic states. The definitions are the same as in Table II.

Transition	γ	s	$\langle \mid r^2 \mid \rangle_{\text{SC}}$	$\langle \mid r^2 \mid \rangle_{\text{ASC}}$	$\langle \mid r^2 \mid \rangle_{\text{EK}}$	Percentage difference
10*s*-9*d*	0.3167	1	5468.6	5468	5453.9	0.25
9*d*-10*s*	0.3167	-1	8755.1	8754.8	8754.6	0.002
8*s*-7*d*	0.4018	1	1949.1	1947.6	1988.6	0.5
7*d*-8*s*	0.4018	-1	3548.7	3546.9	3549.2	0.06
31*s*-29*d*	0.1001	2	-1.3285×10^5	-1.3286×10^5	-1.3288×10^5	0.02
29*s*-31*d*	0.1001	-2	-1.5084×10^5	-1.5083×10^5	-1.5089×10^5	0.04

We write

$$\phi_2^{\pm 2}(\nu l,\nu' l')=\phi_2^{\pm 2}(s,\gamma;l_c)=\sum_{p=0}^{3}\gamma^p Q_p^{(2)}(s) , \tag{52}$$

where the functions $Q_p^{(2)}(s)$ are supposed to be dependent only on s. The functions $Q_p^{(2)}(s)$ are deduced from values of the quadrupole radial integrals between states with $\Delta l=\pm 2$, computed in the region of ν and ν', where we can use the program of Edmonds and Kelly.[9] The method is identical to that which we used in the dipole case.[7,8] The formulas which have been used are given in Appendix C.

We find, as in the hydrogenic case, that the even functions are identical for $\Delta l=0$ and $\Delta l=\pm 2$, when the expansion is truncated after the term in γ^3; we write these functions Q_0 and Q_2. We have checked the values given by Eq. (52) against those obtained from the method of Edmonds and Kelly[9] in Table V. The functions $Q_0(s)\cdots Q_3(s)$ are shown in Fig. 2.

C. Nonhydrogenic case. JWKB-QD method

Davydkin and Makarenko[13] obtained analytic expressions of quadrupole matrix elements for $\Delta l=\pm 2$ in terms of Anger functions. The quadrupole radial integral may be written, using the same definitions of l_c, ν_c, and γ, as in the first two methods as

$$\langle \nu l \mid r^2 \mid \nu' l'\rangle=\frac{\nu_c^4}{s^2}\left[\frac{s\sin(\pi s)}{\pi}(\epsilon-1)^2+\epsilon s[\mathcal{J}_{s-1}(-\epsilon s)-\mathcal{J}_{s+1}(-\epsilon s)]+\frac{s}{2}(2-\epsilon^2)[\mathcal{J}_{s-2}(-\epsilon s)-\mathcal{J}_{s+2}(-\epsilon s)]\right.$$
$$\left.-\frac{\gamma}{2}s[\mathcal{J}_{s-2}(-\epsilon s)+\mathcal{J}_{s+2}(-\epsilon s)]+\epsilon s[\mathcal{J}_{s-1}(-\epsilon s)+\mathcal{J}_{s+1}(-\epsilon s)]\right] . \tag{53}$$

Using recurrence relations between Anger functions, the function $\phi_2^{\pm 2}$ deduced from Eqs. (4) and (53) is given by

$$\phi_2^{\pm 2}(\nu l,\nu' l')=\phi_2^{\pm 2}(s,\gamma;l_c)=\frac{2}{5\epsilon^4 s^2}\left[\left[2\epsilon s(\epsilon^2-1)[\mathcal{J}_{s-1}(-\epsilon s)-\mathcal{J}_{s+1}(-\epsilon s)]+\epsilon^2 s\frac{\sin(\pi s)}{\pi}(\epsilon-1)^2\right.\right.$$
$$\left.+\epsilon(2-\epsilon^2)[\mathcal{J}_{s+1}(-\epsilon s)+\mathcal{J}_{s-1}(-\epsilon s)]\right]$$
$$+\gamma\left[\epsilon s(1-\epsilon^2)[\mathcal{J}_{s+1}(-\epsilon s)+\mathcal{J}_{s-1}(-\epsilon s)]\right.$$
$$\left.\left.-\epsilon[\mathcal{J}_{s-1}(-\epsilon s)-\mathcal{J}_{s+1}(-\epsilon s)]+\epsilon(2+\epsilon)\frac{\sin(\pi s)}{\pi}\right]\right] . \tag{54}$$

We choose the same definitions for l_c, ν_c, and γ as in the first two methods. The MacLaurin series of $\phi_2^{\pm 2}$ in terms of γ gives the same results as the correspondence principle when s is an integer, and, otherwise, the same results as the extrapolation method.

We find for the even functions $Q_0^{(2)}(s)$ and $Q_2^{(2)}(s)$ the same formulas as when $\Delta l=0$; we thus write

$$Q_0^{(2)}(s)=Q_0^{(0)}(s)=Q_0(s)=-\frac{6}{5s}g_1(s) , \tag{55a}$$

$$Q_2^{(2)}=Q_2^{(0)}(s)=Q_2(s)=-\frac{3}{4}\left[\frac{6}{5s}g_1(s)+g_0(s)\right] . \tag{55b}$$

The odd functions may be written

$$Q_1^{(2)}(s)=Q_1(s)=-\frac{2}{5s^2}[\mathcal{J}_{s-1}(-s)-\mathcal{J}_{s+1}(-s)]$$
$$+\frac{6}{5}\frac{\sin(\pi s)}{\pi s^2} \tag{56a}$$

TABLE V. Quadrupole radial integrals $|\Delta l|=2$ between nonhydrogenic states. The definitions are the same as in Tables I and IV.

Transition	γ	s	$\langle \lvert r^2 \rvert \rangle_{\text{EXT}}$	$\langle \lvert r^2 \rvert \rangle_{\text{AEXT}}$	$\langle \lvert r^2 \rvert \rangle_{\text{EK}}$	Percentage difference
30.4*s*-29.6*d*	0.100 02	0.8	1.0227×10^6	1.0225×10^6	1.0227×10^6	0.02
29.6*s*-30.4*d*	0.100 02	−0.8	1.1375×10^6	1.1373×10^6	1.1375×10^6	0.02
7.4*s*-6.6*p*	0.429 97	0.8	2386.5	2386.4	2384.5	0.08
6.6*s*-7.4*p*	0.429 97	−0.8	3790.7	3789.4	3810.0	0.5
30.6*s*-29.4*d*	0.100 04	1.2	3.4110×10^5	3.4103×10^5	3.4110×10^5	0.02
29.4*s*-30.6*d*	0.100 04	−1.2	4.2371×10^5	4.2359×10^5	4.2372×10^5	0.03
7.6*s*-6.4*d*	0.431 74	1.2	642.66	642.61	645.54	0.4
6.4*s*-7.6*d*	0.431 74	−1.2	1657.0	1657.0	1672.2	0.9
30.9*s*-29.1*d*	0.100 09	1.8	-1.2929×10^5	-1.2921×10^5	-1.2929×10^5	0.06
29.1*s*-30.9*d*	0.100 09	−1.8	-1.3140×10^5	-1.3129×10^5	-1.3139×10^5	0.08
7.9*s*-6.1*d*	0.435 57	1.8	−309.64	−309.53	−307.32	0.7
6.1*s*-7.9*d*	0.435 57	−1.8	−311.77	−311.31	−314.92	1

or

$$Q_1(s)=-\frac{6}{5s}g_0(s)+\frac{6}{5}\frac{\sin(\pi s)}{\pi s^2}\,, \tag{56b}$$

$$Q_3^{(2)}(s)=Q_3(s)=\frac{1}{2}\left[\frac{s}{2}Q_0(s)+Q_1(s)\right] \tag{57a}$$

or

$$Q_3(s)=-\frac{1}{2}\left[\frac{3}{5}g_1(s)+\frac{6}{5s}g_0(s)-\frac{6}{5}\frac{\sin(\pi s)}{\pi s^2}\right]. \tag{57b}$$

We can see that the function $\phi_2^{\pm 2}$ and the quadrupole radial integral may be calculated using only functions $g_0(s)$ and $g_1(s)$. The function $\phi_2^{\pm 2}$ takes the form

$$\phi_2^{\pm 2}(s,\gamma;l_c)=-\left[Fg_0(s)+Gg_1(s)-H\frac{6}{5}\frac{\sin(\pi s)}{\pi s^2}\right], \tag{58a}$$

where

$$F=\gamma\frac{6}{5s}+\gamma^2\frac{3}{4}+\gamma^3\frac{3}{5s}\,, \tag{58b}$$

$$G=\frac{6}{5s}+\gamma^2\frac{9}{10s}+\gamma^3\frac{3}{10}\,, \tag{58c}$$

$$H=\gamma+\frac{\gamma^3}{2}\,. \tag{58d}$$

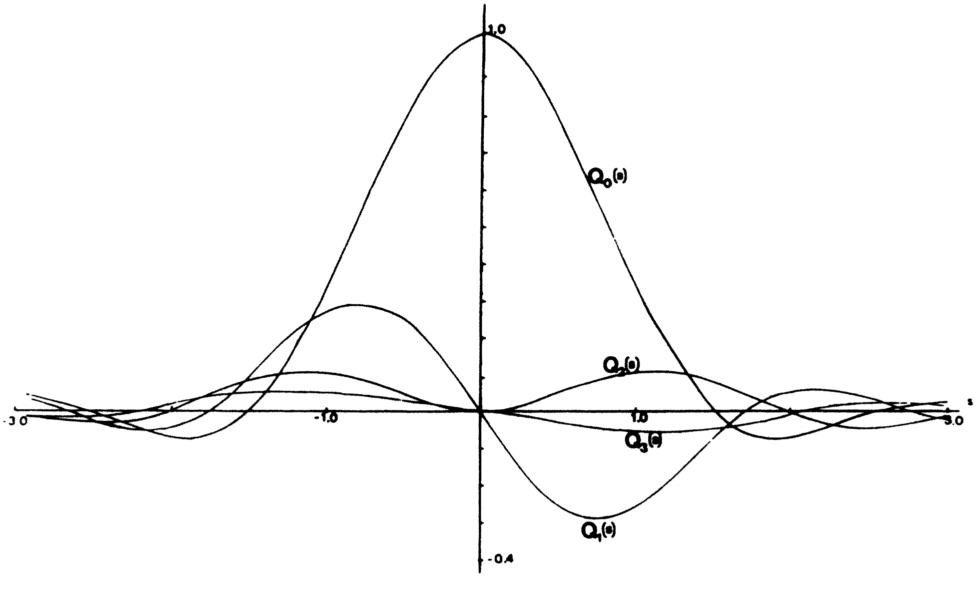

FIG. 2. Graphs of the functions $Q_0(s)\cdots Q_3(s)$.

We have checked the values of quadrupole radial integrals obtained using Eqs. (58a)–(58d) against the exact values of Edmonds and Kelly.[9] We obtain good agreement between the exact and approximated results.

The functions Q approximated by either Bessel or Anger functions are almost identical to extrapolated functions; in other words, we have the same number of significant figures in both cases. If we set Q_A as an approximate value in terms of Anger functions and Q_N as an extrapolated (or "exact") value of functions Q, some measure of the error is given by the number

$$\beta_i = \max |\, Q_N(s) - Q_A(s)\,| \,, \quad 0 \leq s \leq 3$$

where $i = 1,2,3$ is the order of the function Q:

$$\beta_0 = \beta_1 = 1 \times 10^{-6} \,,$$

$$\beta_2 = \beta_3 = 1 \times 10^{-5} \,.$$

The numerical values of the functions Q_0, Q_1, Q_2, and Q_3 for $s = 0,(0.1)3$, calculated using exact matrix elements with the equations of Appendixes B and C, are available from the authors. The same precision is obtained when the functions Q_i are calculated in terms of Anger functions ($i \leq 3$).

Furthermore, better precision may be obtained when terms in γ^4 and γ^5 are introduced. The functions $Q_4^{(2)}(s)$ and $Q_5^{(2)}(s)$ are also functions of $g_0(s)$ and $g_1(s)$, but we observe that the odd functions $Q_4^{(0)}(s)$ and $Q_4^{(2)}(s)$ are not identical. We find

$$Q_4^{(0)}(s) = -\frac{3}{8}\left[\frac{9}{5s}g_1(s) + \frac{11}{4}g_0(s) - \frac{5}{4}\frac{\sin(\pi s)}{\pi s}\right] , \tag{59}$$

$$Q_4^{(2)}(s) = -\frac{3}{8}\left[\frac{1}{s}g_1(s) + \frac{23}{20}g_0(s) - \frac{57}{20}\frac{\sin(\pi s)}{\pi s}\right] , \tag{60}$$

$$Q_5^{(2)}(s) = -\tfrac{3}{4}\left[\tfrac{1}{5}g_1(s) + \frac{3}{4}\left[\frac{2}{5s} + \frac{s}{15}\right]g_0(s)\frac{9}{10}\frac{\sin(\pi s)}{\pi s^2}\right] . \tag{61}$$

V. CONCLUDING REMARKS

Using Heisenberg's form of the correspondence principle in the hydrogenic case, our extrapolation method,[7,8] and the JWKB-QD method[10–13] in the nonhydrogenic case, we have shown that electric dipole and quadrupole radial integrals between atomic Rydberg states $\nu l, \nu' l'$ may be calculated very easily in terms of two functions only of s: $g_0(s)$ and $g_1(s)$. The expansion which is used to calculate radial integrals can be extended as far as any wanted order p; the method is then valid provided the Coulomb approximation is justified.

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APPENDIX A: ANGER FUNCTIONS. DEFINITION AND RECURRENCE FORMULAS

The definition of the Anger function $\mathcal{J}_\Delta(s)$ is suggested by Bessel's integral and is given by

$$\mathcal{J}_\Delta(x) = \frac{1}{\pi}\int_0^\pi \cos(\Delta\theta - x\sin\theta)\,d\theta \,. \tag{A1}$$

This function obviously reduces to $J_n(x)$ when Δ has the integral value n.

The recurrence formulas which are satisfied by the functions of Anger and which we use in that paper[11] are

$$\mathcal{J}_{\Delta-1}(x) - \mathcal{J}_{\Delta+1}(x) = 2\mathcal{J}'_\Delta(x) \,, \tag{A2}$$

$$\mathcal{J}_{\Delta-1}(x) + \mathcal{J}_{\Delta+1}(x) = \frac{2\Delta}{x}\mathcal{J}_\Delta(x) - 2\frac{\sin(\pi\Delta)}{\pi x} \,, \tag{A3}$$

$$\mathcal{J}''_\Delta(x) + \frac{1}{x}\mathcal{J}'_\Delta(x) + \left[1 - \frac{\Delta^2}{x^2}\right]\mathcal{J}_\Delta(x) = \frac{x-\Delta}{\pi x^2}\sin(\pi\Delta) \,. \tag{A4}$$

Numerical computation. Anger functions have been computed using an adaptive integrator especially suited to an oscillating nonsingular integrand.

APPENDIX B: NUMERICAL COMPUTATION OF THE FUNCTIONS $Q_0^0(s)$ AND $Q_2^0(s)$

We may write without ambiguity

$$\phi_2^0(\nu l, \nu' l) = \phi_2^0(\gamma^2, s; l) \,,$$

where γ^2 and s have been defined above. The values of the functions $Q_0^0(s)$ and $Q_2^0(s)$ at chosen values of s may be computed from those of $\phi_2^0(s,\gamma^2;l)$ if the latter is computed for sufficiently small values of γ^2 so that the contribution of degree 4 and higher in γ may be neglected.

We have found that it is necessary to take values of ν_c of at least 25. We choose two different values l_1 and l_2 of l, while keeping ν_c fixed. Defining l_{c1}, l_{c2}, γ_1^2, and γ_2^2 as above, we find

$$Q_0^0(s) = \frac{1}{l_{c2}^2 - l_{c1}^2}[\,l_{c2}^2\phi_2^0(\gamma_1^2, s; l_1) - l_{c1}^2\phi_2^0(\gamma_2^2, s, l^2)\,] \,, \tag{B1}$$

$$Q_2^0(s) = \frac{1}{\gamma_2^2 - \gamma_1^2}[\,\phi_1^0(\gamma_2^2, s; l_2) - \phi_2^0(\gamma_1^2, s; l_1)\,] \,. \tag{B2}$$

It is advantageous to take $l_1 = 1$ and $l_2 = 2$, which gives $l_{c1}^2 = \frac{5}{3}$ and $\gamma_1^2 = 4/3\nu_c^2$, $l_{c2}^2 = \frac{17}{3}$ and $\gamma_2^2 = 13.6/3\nu_c^2$.

APPENDIX C: NUMERICAL COMPUTATION OF THE FUNCTIONS $Q_0^2(s), \ldots, Q_3^2(s)$

The method is the same as that described in Appendix B. But calculations are done, as in the dipole case, on two functions,

$$\phi_2^+(\gamma,s;l_c)=\tfrac{1}{2}[\phi_2(\gamma,s;l_c)+\phi_2(\gamma,-s;l_c)] \; , \tag{C1}$$

$$\phi_2^-(\gamma,s;l_c)=\frac{1}{2\gamma}[\phi_2(\gamma,s;l_c)-\phi_2(\gamma,-s;l_c)] \; . \tag{C2}$$

We have then, with an error of order γ^4,

$$\phi_2^+(\gamma,s;l_c)=Q_0(s)+\gamma^2 Q_2(s) \; , \tag{C3}$$

$$\phi_2^-(\gamma,s;l_c)=Q_1(s)+\gamma^2 Q_3(s) \; . \tag{C4}$$

We choose two different values l_1, l_2 of l_c while keeping ν_c and Δl fixed. Defining

$$\gamma_1=\Delta l\frac{l_1}{\nu_c}, \quad \gamma_2=\Delta l\frac{l_2}{\nu_c} \; ,$$

we find

$$Q_0(s)=\frac{1}{l_2^2-l_1^2}[l_2^2\phi_2^+(\gamma_1,s;l_1)-l_1^2\phi_2^+(\gamma_2,s;l_2)] \; , \tag{C5}$$

$$Q_1(s)=\frac{1}{l_2^2-l_2^2}[l_2^2\phi_2^-(\gamma_1,s;l_1)-l_1^2\phi_2^-(\gamma_2,s;l_2)] \; , \tag{C6}$$

$$Q_2(s)=\frac{1}{\gamma_2^2-\gamma_1^2}[\phi_2^+(\gamma_2,s;l_2)-\phi_2^+(\gamma_1,s;l_1)] \; , \tag{C7}$$

$$Q_3(s)=\frac{1}{\gamma_2^2-\gamma_1^2}[\phi_2^-(\gamma_2,s;l_2)-\phi_2^-(\gamma_1,s;l_1)] \; . \tag{C8}$$

It is advantageous to choose $l_1=\frac{3}{2}$ and $l_2=\frac{5}{2}$.

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