

Radial Matrix Elements of Hydrogen Atom and the Correspondence Principle

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Abstract. Radial dipole matrix elements having astrophysical importance have been computed for highly excited states of hydrogen atom. Computation is based on Heisenberg's form of correspondence principle for Coulomb potential. Particular attention has been paid to the choice of classical analogue (n_c) of principal quantum number (n). The computed radial matrix elements are in good agreement with quantum mechanical results. Further, radial matrix elements for few transitions involving high n neighboring states of hydrogen atom are presented.

Key words. Hydrogen excited states—radial matrix element—correspondence principle.

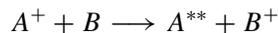
1. Introduction

In the astrophysical environment, high Rydberg atoms are formed with a wide range of values of the principal quantum number n by radiative recombination process. The availability of such high n Rydberg atoms is basically found in the diffuse interstellar gas, molecular clouds, planetary nebulae, and other sources. The interstellar medium is the most appropriate environment because it is subjected to ultra violet radiation and X-rays from extra galactic objects.

We have noticed sufficient progress and exploring interest on highly excited Rydberg atoms theoretically as well as experimentally from mid 1970s to 1990. Review articles describe (Stebbins 1976; Metcalf 1980; Kleppner *et al* 1981) the high n Rydberg atoms, its availability, production, its spectras, and importance in astrophysics (Dupree & Goldberg 1970; Dalgarno 1982). It is very interesting for example, to see a Rydberg atom where the excited electron has a principal quantum number $n \cong 70$, its orbital radius is 0.27×10^{-6} m which has the same size as a typical animal cell.

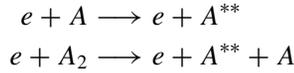
The basic methods of formation of highly excited Rydberg atoms are as follows:

- (i) Charge transfer between A and B atom



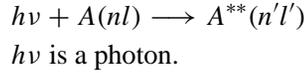
where A^{**} is high n Rydberg atoms.

(ii) Electron impact excitation method



where e is an electron.

(iii) Photon impact method



A highly excited Rydberg atom can be considered as an ion core and an electron far away revolving lazily around in a slow orbit like a distant planet in the solar system. As the electron orbit diameter grows rapidly, its energy also decreases rapidly. Currently, selective excitation to a particular high n state has become possible by the availability of tunable dye LASER. As a result, theoretical calculations involving transition matrix elements, radiative life times, oscillator strengths, etc. have become important to support experimental results concerning high n, l states of Rydberg atoms, which were not available earlier.

Theoretical calculations concerning high n Rydberg states (i.e., $n \longrightarrow \infty$) for any atom based on quantum mechanics becomes difficult, cumbersome, and very time consuming because it involves long series calculations and computations of the product of two long series where proper choice (Gounand 1979) has to be imposed for the upper limit of the series to terminate it. For example, radial matrix element calculation for high n states, needs proper choice for the cut off value of the upper limit of Laguerre Polynomials to get approximate results. Therefore, the best compromise between computation time and long series calculation is the correspondence principle. This principle is more convenient and the best choice to handle high n states in the situation $\Delta E \longrightarrow 0$, $\Delta n \longrightarrow 0$, and $n \longrightarrow \infty$.

2. Theory

In the classical picture, we can imagine that, in a hydrogen atom the electron is revolving around in an elliptical path keeping the nucleus at one of its focii. The eccentricity is ϵ , and a is the semi axis of the ellipse. In the successive excited states of hydrogen atom, correspondence principle can be applied for $n \longrightarrow \infty$, $\Delta E \longrightarrow 0$, $\Delta n \longrightarrow$ very small.

2.1 Correspondence principle in general

The classical theory of action and angle variables (Percival 1974) can be written as

$$I = \frac{1}{2\pi} \oint pdq \quad \text{and} \quad W = \frac{\partial}{\partial I} \int p(I)dq,$$

where q and p are the initial values of position and momentum.

$W = \omega t + \text{constant}$, with ω being the classical frequency.

Here, Sommerfield assumed that $I = n\hbar$, where n is an integer, so that the energy of the system is quantized.

Statement of the Correspondence Principle:

In the limit $n \rightarrow \infty$ and $\Delta n \rightarrow \text{very small}$, $\Delta E \rightarrow 0$, the observed quantum frequency

$$\omega_{nn'} = (E_n - E_{n'})/\hbar \rightarrow \Delta n \omega,$$

where $\Delta n = n' - n$, $\omega = \text{classical frequency}$.

2.2 Heisenberg's form of correspondence principle for radial matrix element

Statement:

This principle (Percival 1974) states that the quantal matrix elements between the quantal states n and n' of the dynamical variable q tends to coincide with the classical Fourier components q_s .

If we write the position coordinate $q(t)$ in terms of Fourier coefficient then

$$q(t) = \sum_s q_s \exp(is\omega t)$$

where q_s is the Fourier coefficient, and hence the quantal matrix element between n and n' states can be written as

$$\langle n | q(t) | n' \rangle = q_s. \quad (1)$$

Naccache (1972) expands the position coordinates (x, y, z) in the angle variables w, ψ, ϕ as follows

$$x(w, \psi, \phi) = \sum_{s, \Delta l, \Delta m} x_{n, l, m}^{n+s, l+\Delta l, m+\Delta m} \exp i(sw + \Delta l \psi + \Delta m \phi), \quad (2)$$

for x, y components, $\Delta l = \pm 1$, $\Delta m = \pm 1$,

for z components, $\Delta l = \pm 1$, $\Delta m = 0$.

Naccache wrote the three matrix elements as

$$\langle n, l, m | x | n + s, l + \Delta l, m + \Delta m \rangle = \Delta l / 4(1 + m \Delta m / l \Delta l) R_{n, l}^{n+s, l+\Delta l}, \quad (3)$$

$$\langle n, l, m | y | n + s, l + \Delta l, m + \Delta m \rangle = -i \Delta m \Delta l / 4(1 + m \Delta m / l \Delta l) R_{n, l}^{n+s, l+\Delta l}, \quad (4)$$

$$\langle n, l, m | z | n + s, l + \Delta l, m + \Delta m \rangle = -i / 2(1 - m^2 / l^2) R_{n, l}^{n+s, l+\Delta l}, \quad (5)$$

where

$$R_{n, l}^{n+s, l+\Delta l} = a \Delta l / s \left\{ J'_s(s\epsilon) + \Delta l (1 - \epsilon^2)^{\frac{1}{2}} / \epsilon J_s(s\epsilon) \right\} \quad (6)$$

is the corresponding classical dipole matrix element between n, l and $n + s, l + \Delta l$ states, a is the semi axis of the elliptic orbit, ϵ is the eccentricity of the ellipse, and $J_s(s\epsilon)$ is the Bessel function.

Naccache has written equation (6) in a better form as

$$R_{n,l}^{n+s,l+\Delta l} = (n_c^2/2s) \Delta l \{(1 + l_c \Delta l/n_c)J_{s-1}(s\epsilon) + (1 - l_c \Delta l/n_c)J_{s+1}(s\epsilon)\}. \quad (7)$$

Percival and Richards (unpublished) wrote the square of $(R_{n,l}^{n,l'})$ as follows

$$(R_{n,l}^{n,l'})^2 = (n_c^2/2s)^2 \{(1 + l_c \Delta l/n_c)J_{s+1}(s\epsilon) - (1 - l_c \Delta l/n_c)J_{s-1}(s\epsilon)\}^2, \quad (8)$$

where n_c and l_c are the classical analogue of principle quantum number n and orbital quantum number l , $s = n - n'$, $\Delta l = l' - l$,

$$n_c = n(n - s)/(n - s/2) = 2nn'/(n + n'), \quad \text{and } l_c = \max(l, l'),$$

$\epsilon = (1 - l_c^2/n_c^2)^{1/2}$ = eccentricity of the elliptic orbit in which the electron of the hydrogen atom is revolving, and $J_s(s\epsilon)$ is the Bessel function.

2.3 Choices on n_c and l_c

There are infinite number of valid choices on n_c and l_c .

Choosing $l_c = l$ and $n_c = \bar{n}$, results can be very close to quantum mechanical results.

Menzel (1968, 1969) had chosen $n_c = n'(1 + 3s/n')$ and $n_c = n'\{1 + 3s/n' + A(s)/(n')^2\}$ where $A(s)$ is a tabulated function of s .

Naccache's choice (Naccache 1972) is $n_c = n(n - s)/(n - s/2) = 2nn'/(n + n')$ and $l_c = \max(l, l')$.

2.4 Introduction of the new choice on n_c in the present work

In the present work, we introduce the new choice on the classical analogue n_c as $n_c = n' \exp(s/2n)$ where n and n' are the initial and the final states and $s = n - n'$. This new choice of n_c , compared to $(n_c)_{\text{naccache}}$, brings the values of $(R_{n,l}^{n,l'})^2$ very close to quantum mechanical results. Here we follow the symbols $(n_c)_{\text{naccache}}$ for $n_c = 2nn'/(n + n')$ and $(n_c)_{\text{presentchoice}}$, $(n_c)_{\text{presentwork}}$ or $(n_c)_{\text{introduced}}$, for $(n_c) = n' \exp(s/2n)$ throughout the whole discussion and particularly in the tables of results.

The basic reason to choose a particular mathematical form of n_c as $(n_c) = n' \exp(s/2n)$ is as follows:

In this work, we concentrate on the radial transition matrix element concerning highly excited neighbouring states of hydrogen atom with small s values. This requirement is implicit in the mathematical form of n_c . As radial matrix elements are dependent on n_c^2 , so the value of n_c is very sensitive to get accurate results for the radial matrix elements. Keeping in mind the sensitivity of radial matrix element on n_c , the exponential power $s/2n$ and the multiplication factor n' has been so chosen that for small values of s , and by adjusting with the multiplication factor n' , it will lead more accurate results for n_c which ultimately lead to close results with the quantum mechanical

values of radial matrix element. On the contrary, if s increases, $\exp(s/2n)$ becomes very large, which leads to much inaccuracy and large variation from quantum mechanical values of radial matrix element, which has been shown in the results. As radial matrix element depends on n_c^2 and n_c is very sensitive on s , so the mathematical form $n_c = n' \exp(s/2n)$ is justified for high n neighbouring states.

Naccache had calculated radial matrix element with the choice $n_c = n(n-s)/(n-s/2)$ which leads to very close results with the quantum mechanical values of radial matrix element, so it is our advantage to check our values of n_c with Naccache's values. Here, we have found that the exponential form of presentation of n_c closely tallies with the Naccache's form of n_c . Further, crosscheck has been done for the eccentricity, which also is highly satisfactory.

Therefore, we guess that our choice of n_c will be very helpful for calculating radial matrix element for very high n neighbouring states and also for the calculation of oscillator strength.

3. Calculations

The square of the radial dipole matrix elements, i.e., $(R_{n,l}^{n'l'})^2$ has been calculated in the present work. We have taken equation (8) for this calculation. The new introduced choice of n_c has been incorporated in this calculation keeping the choice of l_c by Naccache the same i.e., $l_c = \max(l, l')$. Equation (8) slightly differs from Naccache (1972) because Percival & Richards (unpublished) reported that s of Naccache (1972) is the negative of that used by them because there is an error in a sign of the result in Naccache's paper.

In quantum mechanical calculations of radial dipole matrix elements, the product of two Laguerre polynomials appears frequently which is very difficult to solve when $n \rightarrow \infty, n' \rightarrow \infty$.

Particularly the choice (Gounand 1979) for the cutoff criterion is imposed to terminate the series quickly for an approximate result. In contrast with the quantum mechanical calculations, the computation of Bessel functions $J_s(s\epsilon)$ is convenient and easier to handle even for very high n states.

Since classical analogue of principle quantum number n_c is represented in the exponential form in our new introduction of choice, we guess that apart from the transition between neighbouring states, if s is large, the difference of values between quantum mechanical and correspondence principle values for $(R_{n,l}^{n'l'})^2$ becomes large. Because when s is large, we take a departure from the condition of applying the correspondence principle for highly excited states. We therefore, concentrate on calculations based on closely lying neighbouring excited states of hydrogen where s is very small.

4. Results and discussion

In general, when $n \rightarrow \infty, n' \rightarrow \infty$ and $s = n - n'$ is very small, $\Delta E \rightarrow 0$, correspondence principle is the meaningful choice for the transition between successive stationary states which can be considered as quasi classical states. In the new choice of $n_c = n' \exp(s/2n)$ introduced here, s is in the exponential power and so s is very sensitive for calculating n_c . Therefore, calculations have been restricted for high n neighbouring states of hydrogen atom.

4.1 Comparison on the choice of n_c

The dependence of $(R_{n,l}^{n'l'})^2$ on n_c is $(n_c)^4$.

So, considerable change of n_c i.e., Δn_c will matter much for such a type of calculation. Since the choice $(n_c)_{\text{naccache}}$ reproduces very close agreement to quantum mechanical calculations, we compare $(n_c)_{\text{presentwork}}$ and $(n_c)_{\text{naccache}}$ in Table 1.

Table 1. Comparison of $(n_c)_{\text{naccache}}$ and $(n_c)_{\text{presentchoice}}$.

Transition ($n \rightarrow n'$)	$(n_c)_{\text{naccache}}$	$(n_c)_{\text{presentchoice}}$	% difference
8 \rightarrow 7	7.46	7.45	0.13
20 \rightarrow 19	19.48	19.48	0
100 \rightarrow 99	99.497	99.496	$\sim 10^{-5}$
500 \rightarrow 499	499.499	499.499	0

In table 1, we see that as we move from the transition $n = 8 \rightarrow 7$ to transition between very highly excited neighbouring states i.e., $n = 20 \rightarrow 19$, $100 \rightarrow 99$, $500 \rightarrow 499$, the % difference between $(n_c)_{\text{naccache}}$ and $(n_c)_{\text{introduced}}$ is in between 0 and 0.13. Therefore, such a choice on n_c will yield very good results for computation of $(R_{n,l}^{n'l'})^2$. Regarding l and l' also we restrict ourselves to the neighbouring l states where Δl is very small.

4.2 Comparison between neighbouring and far-off states

If we move apart from neighbouring states transitions to far off states, s value increases. since s is in the exponential power, the introduced choice of n_c , is very sensitive on s . We have seen poor agreement of a result for the calculation of $(R_{n,l}^{n'l'})^2$ with the quantum mechanical results for the transition $n = 13, l = 7 \rightarrow n' = 20, l' = 8$. So, in Table 2 we compare $(n_c)_{\text{presentchoice}}$ with $(n_c)_{\text{naccache}}$ for upward and downward

Table 2. Comparison of $(n_c)_{\text{naccache}}$ and $(n_c)_{\text{presentchoice}}$ for the upward and downward transition from the level $n = 13$.

Transition from $n = 13$	$(n_c)_{\text{naccache}}$	$(n_c)_{\text{presentchoice}}$	% difference
Upward transition \uparrow			
13 \rightarrow 14	13.48	13.47	0.07
13 \rightarrow 15	13.92	13.89	0.21
13 \rightarrow 16	14.34	14.25	0.62
13 \rightarrow 20	15.75	15.28	2.98
Downward transition \downarrow			
13 \rightarrow 12	12.48	12.47	0.08
13 \rightarrow 11	11.91	11.88	0.03
13 \rightarrow 10	11.30	11.22	0.70
13 \rightarrow 6	8.21	7.85	4.38

Table 3. Comparison of the values of $(R_{n,l}^{nl})^2$ based on quantum mechanical calculations and correspondence principle with different choice of n_c .

Transition	$(R_{n,l}^{nl})^2$ QM values	$(R_{n,l}^{nl})^2_{\text{naccache}}$ with choice $(n_c = n - s/2)$	%diff	$(R_{n,l}^{nl})^2_{\text{naccache}}$ with choice $n_c = 2nl/(n + nl)$	%diff	$(R_{n,l}^{nl})^2_{\text{presentwork}}$ with choice $n_c = n/\exp(s/2n)$	%diff
$2s \rightarrow 3p$	9.393	11.022	17.34	9.270	1.30	8.974	4.46
$3s \rightarrow 5p$	72.553	76.395	5.30	73.181	0.86	71.505	1.44
$6s \rightarrow 7p$	274.19	281.22	2.56	275.25	0.38	272.27	0.7
$4p \rightarrow 5d$	121.86	127.86	4.92	123.18	1.08	120.49	1.12
$4d \rightarrow 5f$	197.83	207.00	4.63	200.46	1.33	196.65	0.596
$13, 7 \rightarrow 20, 8$	39.5	47.18	19.4	37.96	3.89	32	18.98

transition between the neighbouring states from the level $n = 13$. Comparison indicates that when s is small, the percentage difference between present choice of n_c and Naccache's is $< 0.75\%$, but when s is large, % difference for upward transition is around 3% and for downward transition it is around 4%. This clearly indicates that this choice is practically concentrated on the neighbouring states transition for the highly excited Rydberg states.

4.3 Comparison of the values of $(R_{n,l}^{n'l'})^2$

In Table 3 the square of the radial matrix elements of hydrogen i.e., $(R_{n,l}^{n'l'})^2$ based on quantum mechanical calculations is compared with the calculation based on correspondence principle with various choices of n_c and the new choice introduced for n_c in the present work. In the transition presented in Table 3, $|s| = 1$, $\Delta l = l' - l = 1$ for the five transitions except the last one where $|s| = 7$ and $\Delta l = +1$. Agreement of the results of the present work with quantum mechanical calculation is fairly good. This result reflects that for highly excited states of hydrogen where the transitions involve neighbouring states, the choice of n_c in the present work will yield better results. In the last transition s is large, therefore % difference of $(n_c)_{\text{naccache}}$ and $(n_c)_{\text{presentwork}}$ is also large which leads to poor agreement, because the dependence of $(R_{n,l}^{n'l'})^2$ on n_c is n_c^4 .

4.4 Results for the high n states with the present choice of n_c

In Table 4, we present the values of $(R_{n,l}^{n'l'})^2$ of hydrogen atom. The calculation is based on correspondence principle incorporating our introduced choice on n_c . Comparison has been made between $(n_c)_{\text{naccache}}$ and $(n_c)_{\text{presentchoice}}$, which follows the condition of application of correspondent principle. Here, quantum mechanical values for $(R_{n,l}^{n'l'})^2$ for the given transitions could not be presented because of the non availability of theoretical data. Our expectation is that these values of $(R_{n,l}^{n'l'})^2$ will tally perfectly with the quantum mechanical calculations for the given states in Table 4.

Table 4. Computed values of $(R_{n,l}^{n'l'})^2$ of hydrogen atom based on the correspondence principle with the introduced choice of n_c have been presented.

Transition	Values of $(R_{n,l}^{n'l'})^2_{\text{presentwork}}$	Comparison of n_c values		
		$(n_c)_{\text{naccache}}$	$(n_c)_{\text{presentwork}}$	% difference
$10s \rightarrow 11p$	1.631×10^3	10.476	10.463	0.12
$20s \rightarrow 19p$	1.3211×10^4	19.487	19.480	0.03
$29s \rightarrow 30p$	8.7318×10^4	29.491	29.487	0.01
$50s \rightarrow 49p$	6.0×10^5	49.494	49.492	0.004

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