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# The hydrogen atom's quantum-to-classical correspondence in Heisenberg's correspondence principle

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**Abstract**

The famous Gordon formula for matrix element $\langle n', l|r|n, l-1\rangle$ is transformed into a new form which can be easily treated when $n'$, $n$ and $l$ are all large. Then its asymptotic expression is derived which turns out to be that obtained from Heisenberg's correspondence principle. Finally, its classical limit form is used to construct classical quantities $x$, $y$ and $z$ representing a singe Keplerian orbit in terms of a Fourier series of time variable $t$.

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The quantum-to-classical correspondence is a question of fundamental importance, and there are not only conceptual but also technical problems involved in various forms of the correspondence. Since the solution to the hydrogen atom laid the cornerstone of quantum mechanics, a close examination of its quantum-to-classical correspondence is always needed in each form of them. This paper aims to present a study of the hydrogen atom's quantum-to-classical correspondence in light of Heisenberg's correspondence principle.

The preliminary form of Heisenberg's correspondence principle clearly presents in the classic work of Heisenberg himself [1]. Let a classical system be quantized semiclassically, i.e. let the classical action $J_k$ be quantized as $J_k = n_k\hbar$ $(n_k = 1, 2, \ldots)$, Heisenberg concluded from empirical facts an approximate identity for a general coordinate $q$ when quantum numbers are large:

$$\int \psi^*_{n+k}(q,t)q\psi_n(q,t)\,\mathrm{d}x = \langle n+k|q|n\rangle \mathrm{e}^{\mathrm{i}(E_{n+k}-E_n)t/\hbar} \approx q_k(n)\mathrm{e}^{\mathrm{i}k\omega(n)t} \tag{1}$$

where $q_k(n)$ is the $k$th Fourier component of classical coordinate $q$ and $\omega(n)$ is the classical frequency [1]. There has been a steady interest in and development of Heisenberg's correspondence principle, mostly related to studies of quantum chaos and/or the Rydberg (highly excited hydrogen-like) atom [2–10]. In modern notion, Heisenberg's correspondence principle can be stated as follows. The matrix element (ME) of an operator with respect to states with quantum numbers $n$ and $m$ is approximately the $(n-m)$th Fourier component of the operator's classical function evaluated on the so-called average quantized torus [9, 10]. For the sake of brevity, the true quantum mechanical ME and that obtained from Heisenberg's correspondence principle are abbreviated to QME and HME respectively.

Owing to its exclusive importance, applications of Heisenberg's correspondence principle to the hydrogen atom attract special attention. Among those successful applications, the fundamental one is the evaluation of the radial ME of the dipole moment ($\hbar = \mu = e = 1$ throughout this paper),

$$\langle n+k, l|r|n, l-1\rangle = \int_0^\infty R_{n+k,l}(r) R_{n,l-1}(r) r^3 \, \mathrm{d}r \qquad (k \neq 0) \tag{2}$$

which is, from Heisenberg's correspondence principle, [3–5],

$$\langle n+k, l|r|n, l-1\rangle = \frac{n_c^2}{k}\left[J_k'(k\epsilon_c) - \frac{\sqrt{1-\epsilon_c^2}}{\epsilon_c} J_k(k\epsilon_c)\right] \qquad (k \neq 0) \tag{3}$$

where $n_c$ is some mean of quantum numbers $n+k$ and $n$; $\epsilon_c = \sqrt{1-(l_c/n_c)^2}$ is the eccentricity; and $l_c$ is some mean of $l$ and $l-1$. It is understandable that, for achieving the best fit to the QME with small quantum numbers, the definitions of mean $n_c$ or $l_c$ in (3) are different from paper to paper [3, 4, 9, 10]. The mean could be, for example, arithmetic, geometric, harmonic, quadratic and reciprocal quadratic [11], and all comparisons are performed *numerically* in the region of the principal quantum number $\leqslant 20$ [3, 12]. However, when $n$, $l$ and $n-l$ are much greater than 1, and $k$ is relatively small, whether the mean is used, we have

$$n_c \approx n \qquad l_c \approx l \qquad \text{and} \qquad \epsilon_c \approx \epsilon = \sqrt{1-(l/n)^2}. \tag{4}$$

Then the HME (3) should well approximate with the following QME (5) which was first obtained by Gordon [13]:

$$\begin{aligned}\langle n', l|r|n, l-1\rangle = {} & (-1)^{n-l}\frac{1}{4(2l-1)!}\sqrt{\frac{(n'+l)!(n+l-1)!}{((n'-l-1)!(n-l)!)}}(4n'n)^{l+1}\frac{(n'-n)^{n'+n-2l-2}}{(n'+n)^{(n'+n)}} \\ & \times\left(F\left(-(n'-l-1), -(n-l); 2l; \frac{-4n'n}{(n'-n)^2}\right) - \left(\frac{n'-n}{n'+n}\right)^2\right. \\ & \left.\times F\left(-(n'-l+1), -(n-l); 2l; \frac{-4n'n}{(n'-n)^2}\right)\right) \qquad (n' \neq n).\end{aligned} \tag{5}$$

As Gordon himself knew [13] and paper [14] emphasized, the Gordon formula can hardly apply to quantitative estimations or direct calculations with large values of $n'$, $n$ and $l$, because all the three parameters and the argument of the hypergeometric function are large. So, there has not yet been any analytical work comparing the two MEs (5) and (3). Filling the gap is the principal goal of this paper.

The key step to simplify the Gordon formula (5) is to use a relation between hypergeometric functions with different arguments $x$ and $1/(1-x)$. For positive integers $-a$, $-b$ and $c$ with

$0 > a \geqslant b$, we have[5]:

$$F(a,b;c;x) = (-1)^a (1-x)^{-a} \frac{\Gamma(c)}{\Gamma(c-a)} \frac{(-b)!}{(a-b)!} F\left(a, c-b; a-b+1; \frac{1}{(1-x)}\right) \tag{6}$$

which can apply to the case $a \leqslant b < 0$ after simply interchanging $a$ and $b$ in the RHS of the identity. By using this relation, the Gordon formula can be transformed into a more convenient form such as

$$\begin{aligned}\langle n', l|r|n, l-1\rangle &= 4^l \left(\frac{n' n}{(n'+n)^2}\right)^{1+l} \left(\frac{-n'+n}{n'+n}\right)^{n-n'} \sqrt{\frac{(l+n')\ (-l+n)!\ (l+n)!}{(l+n)\ (-1-l+n')!\,(-1+l+n')!}} \\ &\times\left[\frac{1}{(l+n')\ \Gamma(-n'+n)}\left(\frac{n'+n}{n'-n}\right)^2 F\left(-1+l-n', l+n; -n'+n; \frac{(n'-n)^2}{(n'+n)^2}\right)\right. \\ &\left.-\frac{(-1+l+n')}{\Gamma(2-n'+n)} F\left(1+l-n', l+n; 2-n'+n; \frac{(n'-n)^2}{(n'+n)^2}\right)\right].\end{aligned} \tag{7}$$

This expression can apply in the case $n > n'$. While in the case $n < n'$, the QME $\langle n', l|r|n, l-1\rangle$ is

$$\begin{aligned}\langle n', l|r|n, l-1\rangle &= 4^l \left(\frac{n' n}{(n'+n)^2}\right)^{1+l} \left(\frac{n'-n}{n'+n}\right)^{n'-n} \sqrt{\frac{(-l+n')\,(-l+n')!\,(l+n')!}{(-l+n)\,(-1-l+n)!\ (l+n)!}} \\ &\left[\frac{1}{(-l+n')\ \Gamma(n'-n)}\left(\frac{n'+n}{n'-n}\right)^2 F\left(l-n, 1+l+n', n'-n, \frac{(n'-n)^2}{(n'+n)^2}\right)\right. \\ &\left.-\frac{(1-l+n')}{\Gamma(2+n'-n)} F\left(l-n, 1+l+n', 2+n'-n, \frac{(n'-n)^2}{(n'+n)^2}\right)\right].\end{aligned} \tag{8}$$

In this paper, we like to give the detailed steps to simplify (7). The same steps can simplify (8). Let $n' = n + k$ with $k \leqslant 1$, the expression (7) is

$$\begin{aligned}\langle n+k, l|r|n, l-1\rangle &= 4^l \left(\frac{n\ (k+n)}{(k+2n)^2}\right)^{1+l} \left(\frac{k}{k+2n}\right)^k \\ &\times\sqrt{\frac{(l+n)\ (k-l+n)!\ (k+l+n)!}{(k+l+n)\,(-1-l+n)!\ (-1+l+n)!}} \\ &\times\left[\frac{1}{(l+n)\ \Gamma(k)} \frac{(k+2n)^2}{k^2} F\left(-1+l-n, k+l+n; k; \frac{k^2}{(k+2n)^2}\right)\right. \\ &\left.-\frac{(-1+l+n)}{\Gamma(2+k)} F\left(1+l-n, k+l+n; 2+k; \frac{k^2}{(k+2n)^2}\right)\right].\end{aligned} \tag{9}$$

The factors in (9) can be rewritten one by one as

$$\left(\frac{n\ (k+n)}{(k+2n)^2}\right)^{1+l} = \frac{1}{4^{l+1}} \left\{\left(1 - \left(\frac{k}{2n}\right)^2 \frac{1}{(1+k/2n)^2}\right)^{l+1}\right\} \approx \frac{1}{4^{l+1}} \tag{10}$$

$$\frac{k}{k+2n} = \frac{k}{(2n)} \left\{\left(1+\frac{k}{2n}\right)^{-1}\right\} \approx \frac{k}{(2n)} \tag{11}$$

[5] Note that the usual literature gives the formula $F(a,b;c;z) = (1-z)^{-a} \frac{\Gamma(c)}{\Gamma(b)} \frac{\Gamma(b-a)}{\Gamma(c-a)} F(a, c-b; a-b+1; \frac{1}{(1-z)}) + (a \rightleftharpoons b)$, which can apply when $|\arg(1-z)| < \pi$, $a-b \neq m$, $(m = 0, 1, 2, 3, \ldots)$ [15,16]. When $m$ is an integer, one can verify the correctness of our formula (6) by direct comparison of the coefficients before $x^u$ $(u = 0, 1, 2, 3, \ldots)$ on both sides of it.

$$\frac{(l+n)\ (k-l+n)!\ (k+l+n)!}{(k+l+n)\,(-1-l+n)!\ (-1+l+n)!}$$
$$= (n\epsilon)^{2(k+1)}\left\{\left(1+\frac{k}{n+l}\right)^{-1}\prod_{i=0}^{k}\left(1+\frac{\mathrm{i}}{n-l}\right)\left(1+\frac{\mathrm{i}}{n+l}\right)\right\} \approx (n\epsilon)^{2(k+1)} \tag{12}$$

$$F\left(-1+l-n, k+l+n; k; \frac{k^2}{(k+2n)^2}\right)$$
$$= (k-1)!\sum_{s=0}^{n-l+1}\frac{(-1)^s}{s!(s+k-1)!}\left(\frac{k\epsilon}{2}\right)^{2s}$$
$$\times\left\{\delta_{s0}+\bar{\delta}_{s0}\left(1+\frac{k}{2n}\right)^{-2s}\prod_{i=0}^{s-1}\left(1-\frac{\mathrm{i}-1}{n-l}\right)\left(1+\frac{\mathrm{i}+k}{n+l}\right)\right\}$$
$$\approx (k-1)!\sum_{s=0}^{n-l+1}\frac{(-1)^s}{s!(s+k-1)!}\left(\frac{k\epsilon}{2}\right)^{2s} \tag{13}$$

$$F\left(1+l-n, k+l+n; k+2; \frac{k^2}{(k+2n)^2}\right)$$
$$= (k+1)!\sum_{s=0}^{n-l-1}\frac{(-1)^s}{s!(s+k+1)!}\left(\frac{k\epsilon}{2}\right)^{2s}$$
$$\times\left\{\delta_{s0}+\bar{\delta}_{s0}\left(1+\frac{k}{2n}\right)^{-2s}\prod_{i=0}^{s-1}\left(1-\frac{\mathrm{i}+1}{n-l}\right)\left(1+\frac{\mathrm{i}+k}{n+l}\right)\right\}$$
$$\approx (k+1)!\sum_{s=0}^{n-l-1}\frac{(-1)^s}{s!(s+k+1)!}\left(\frac{k\epsilon}{2}\right)^{2s} \tag{14}$$

where the approximation holds only when $n$, $l$ and $n-l$ are much greater than 1 and $k$ is relatively small; and

$$\delta_{s0} = \begin{cases} 1 & s=0 \\ 0 & s\neq 0 \end{cases} \qquad \text{and} \qquad \bar{\delta}_{s0} = \begin{cases} 1 & s\neq 0 \\ 0 & s=0. \end{cases}$$

Noting that the resulting series in equations (13) and (14) are the first $(n-l-1)$ and $(n-l+1)$ terms of Bessel functions of integer order $k-1$ and $k+1$ respectively, this can be used to approximate the Bessel function. Since the Bessel function $J_k(z)$ of integer order $k$ consists of an infinite alternating series as $J_k(z) = \sum_{s=0}^{\infty}\frac{(-1)^s}{(k+s)!s!}(\frac{z}{2})^{2s+k}$, the absolute error of using the truncated Bessel function involving only the first $N$ terms to represent the function itself is less than the absolute value of the $(N+1)$th term. We can define a ratio of it to the first term as $|(\frac{z}{2})^{2N+k}((k+N)!N!)^{-1}/(\frac{z}{2})^k(k!N!)^{-1}|$ to estimate the relative error. In our problem, $z \leqslant k+1$. When $n$, $l$ and $n-l$ are much larger than 1, there are $n-l+2$ terms in the series (13), and $n-l$, in (14). The ratio is extremely small. For example, when $N=30$, the error is less than $3.16\times 10^{-11}$; and when $N=100$, the error is less than $5.77\times 10^{-35}$. Then the asymptotic QME expression $\langle n', l|r|n, l-1\rangle$ (8) is

$$\langle n+k, l|r|n, l-1\rangle \approx 4^l\left(\frac{1}{4^{l+1}}\right)\left(\frac{k}{2n}\right)^k (n\,\epsilon)^{(k+1)}$$
$$\times\left[\frac{1}{(l+n)}\frac{(2n)^2}{k^2}\sum_{s=0}^{n-l+1}(-1)^s\frac{1}{s!(k+s-1)!}\left(\frac{k\epsilon}{2}\right)^{2s}\right.$$

$$
\begin{aligned}
&\quad - (-1 + l + n) \sum_{s=0}^{n-l-1} (-1)^s \frac{1}{s!(k+s+1)!} \left(\frac{k\epsilon}{2}\right)^{2s} \Bigg] \\
&= \frac{n\,\epsilon}{4} \left(\frac{2n}{k\epsilon}\right) \Bigg[ \frac{n\,\epsilon^2}{l+n} \sum_{s=0}^{n-l+1} (-1)^s \frac{1}{s!(k+s-1)!} \left(\frac{k\epsilon}{2}\right)^{2s+k-1} \\
&\quad - \frac{n+l-1}{n} \sum_{s=0}^{n-l-1} (-1)^s \frac{1}{s!(k+s+1)!} \left(\frac{k\epsilon}{2}\right)^{2s+k+1} \Bigg] \\
&\approx \frac{n^2}{2k} \left[ \left(1 - \frac{l}{n}\right) J_{k-1}(k\epsilon) - \left(1 + \frac{l}{n}\right) J_{k+1}(k\epsilon) \right] \\
&= \frac{n^2}{k} \left[ J_k'(k\epsilon) - \frac{\sqrt{1-\epsilon^2}}{\epsilon} J_k(k\epsilon) \right]. \qquad (15)
\end{aligned}
$$

In the last step, we used the recursion relations [15], $2J_k'(z) = J_{k-1}(z) - J_{k+1}(z)$ and $(2k/z)J_k(z) = J_{k-1}(z) + J_{k+1}(z)$. If we start from the equation (8), the same expression (15) will be obtained, but with $k \geqslant 1$. So, equation (15) in fact holds true as long as $k$ is a nonzero integer.

From the studies above, we see that when quantum numbers are large and $k$ is small, the QME (5) is in asymptotic agreement with the HME (3). The difference between these two MEs decreases from equations (10) to (14) as $1/N$ $(N = n, l, n-1)$ when $N \to \infty$.

Note that HME (3) was obtained from the semiclassical quantities $x$, $y$ and $z$ expressed in terms of a Fourier series of three angle angles $\omega$, $\theta$ and $\phi$ [2, 3] rather than a single time variable $t$. On one hand, the dependence on angles is rather a geometrical relation, while that on time is rather an evolution equation of time. One cannot directly obtain the latter from the former. On the other hand, the classical limit of expectation values of quantities $x$, $y$ and $z$ in some wavepacket becomes the classical quantities, and the form is not the exact Fourier timeseries $t$ but its Fejér average [17]. It is therefore interesting to construct, from classical limit of the HMEs, the classical quantities $x$, $y$ and $z$ in terms of the exact Fourier series. For our purposes, for a one-dimensional system, we construct a quantity $f_q(t)$; that is,

$$
f_q(t) = \sum_{n'=0}^{\infty} \langle n'|f|n\rangle \exp[\mathrm{i}(E_{n'} - E_n)t/\hbar] = \sum_{k=-n}^{\infty} \langle n+k|f|n\rangle \exp[\mathrm{i}(E_{n+k} - E_n)t/\hbar] \qquad (16)
$$

where the symbol $\sum$ denotes summation over discrete quantum numbers, and the integral over the possible continuous ones. The reason why this quantity is constructed is that Heisenberg's correspondence principle (1) implies the following when the quantum number is large:

$$
f_q(t) \text{ in large quantum number case} \to \text{the classical quantity } f(t) \qquad (17)
$$

where '$\to$' can be replaced by '$=$' in the classical limit $n \to \infty$ [17]. Analogously, for the hydrogen atom, equation (16) can be written as

$$
\begin{aligned}
f_q(t) &= \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \langle n'l'm'|f|nlm\rangle \exp[\mathrm{i}(E_{n'} - E_n)t/\hbar] \\
&= \sum_{k=-n+1}^{\infty} \left( \sum_{l'=0}^{n+k-1} \sum_{m'=-l'}^{l'} \langle (n+k)l'm'|f|nlm\rangle \right) \exp[(\mathrm{i}E_{n+k} - E_n t)/\hbar]. \qquad (18)
\end{aligned}
$$

Let $f = x$, $y$ and $z$, once the result on radial ME, $\langle n, l|r|n, l-1\rangle = -3n^2\epsilon/2$ [3], is added, equation (18) immediately leads to in the limit of infinite quantum numbers $n$, $l$ and $m$, while keeping $n\hbar$, $l\hbar$ and $m\hbar$ as classical actions:

$$
\begin{aligned}
\frac{x}{a} &= -\frac{m}{l}\left[-\frac{3}{2}\epsilon + \sum_{k=-\infty,k\neq 0}^{\infty} \frac{1}{k} J_k'(k\epsilon)\exp(\mathrm{i}k\omega t)\right] \\
\frac{y}{a} &= -\frac{\sqrt{1-\epsilon^2}}{\epsilon} \sum_{k=-\infty,k\neq 0}^{\infty} \frac{\mathrm{i}}{k} J_k(k\epsilon)\exp(\mathrm{i}k\omega t) \\
\frac{z}{a} &= \frac{\sqrt{l^2-m^2}}{l}\left[-\frac{3}{2}\epsilon + \sum_{k=-\infty,k\neq 0}^{\infty} \frac{1}{k} J_k'(k\epsilon)\exp(\mathrm{i}k\omega t)\right]
\end{aligned}
\tag{19}
$$

where $a = n^2 a_0$ is the semi-major with $a_0$ the Bohr radius. Now, $x$, $y$ and $z$ in (19) are classical quantities representing a single Keplerian orbit characterized by classical energy $E = E_n$, the angular momentum $J = l\hbar$, its projections along the $z$-axis $J_z = m\hbar$, and the $x$-axis $J_x = \sqrt{l^2 - m^2}\hbar$ [2, 18].

Now we close this paper with the following summary. (1) The famous Gordon formula for ME $\langle n', l|r|n, l-1\rangle$ is transformed into a new form which can be easily treated when $n'$, $n$ and $l$ are all large. Then we have an asymptotic expression which turns out to be that obtained from Heisenberg's correspondence principle. We have noted that the quantum mechanics for the Rydberg atom does not in general converge to the classical mechanics for the Kepler system [19], whereas the QME has excellent classical correspondence. (2) Heisenberg's correspondence principle (1) implies that the classical limit form of QME can be used to reproduce the classical quantity in terms of Fourier series of variable $t$, and such classical quantities $x$, $y$ and $z$ for Keplerian motion are successfully constructed. In fact, we have attempted to study the real part of the constructed quantity $f_q(t)$ in the small quantum number case, results reveal that for some of the one-dimensional unbound systems which only have a continuous spectrum of energy, $f_q(t)$ can sometimes be identical to $f(t)$ [20].

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