Note

On the limiting radial distribution function for hydrogenic orbitals

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An exact reduced limiting expression for the generalized radial distribution function $D_n(r)$ is derived and compared with quantum distributions for various degrees of excitation. It represents the quantum result at large quantum numbers significantly better than a prior empirical representation of the universal reduced distribution and gives a somewhat larger electronic partition function for the hydrogen atom than that based on the previous distribution.

Several years ago a generalized radial distribution function $D_n(r)$ was introduced [1] to characterize the spherically symmetrical function resulting from a summation over all angular momentum states for a given energy. Such a function had attracted attention before, although in less detail [2,3]. It was recognized that it approached a limiting form at large quantum numbers and an empirical, universal reduced form was suggested for the limiting case. This expression was subsequently applied in the calculation of the partition function for the hydrogen atom [4]. The present note gives an explicit expression for the exact limiting function for bound states, compares it with quantum results for increasing quantum numbers, and applies it to the computation of the partition function.

As expected from the correspondence principle, the limiting distribution is the classical result. Because the classical distribution $D(r)dr$ for any orbit is proportional to the time dt spent in the interval between r and $r + dr$ by a particle of velocity $\mathbf{v}$, the result sought is

$$D(r)dr \propto r dr/\mathbf{v} \cdot \mathbf{r} . \quad (1)$$

Therefore, for a given energy

$$E_n = -Z^2/n^2 \quad (2)$$

in atomic units ($\hbar = m = e = 1$) and for a given angular momentum

$$\mathbf{L} = \mathbf{r} \times \mathbf{v}, \tag{3}$$

it follows that

$$D_{n,L}(r) = K_{n,L}/\sqrt{2Z/r - Z^2/n^2 - L^2/r^2}, \tag{4}$$

where the proportionality constant $K_{n,L}$ is independent of angular momentum. If we introduce the reduced variable $\rho = 2Zr/n^2$, the expression for $D_n(r)$, normalized to the orbital degeneracy n^2, is just the sum over all of the components $D_{n,L}(r)$, so that, in view of the $2L$-fold multiplicity of the angular momentum,

$$D_n(r) = \frac{Z\rho}{n\pi}\int_0^n \mathrm{Re}(1/\sqrt{n^2(\rho - \tfrac{1}{4}\rho^2 - L^2)}LdL, \tag{5}$$

whence

$$\begin{aligned} D_n(r) &= \frac{Z}{2\pi}\rho\sqrt{4\rho - \rho^2}, \quad 0 \leqslant \rho \leqslant 4, \\ &= 0 \qquad\qquad\qquad \rho > 4. \end{aligned} \tag{6}$$

It was noted previously that $D_n(r)$ exhibits a maximum value $\approx 0.833Z$ near $r \approx 1.5n^2/Z$. The maximum of the classical representation (6) is 0.827Z at exactly $r = 1.5n^2/Z$. Illustrated in Fig. 1 are plots comparing the limiting distribution with the quantum radial distribution functions derived from hydrogenic orbitals. The present expression gives a significantly more faithful representation of the quantum distributions at large n than does the empirical expression previously suggested [1], particularly in the vicinity of the maximum classical turning point.

One application of the limiting radial distribution function is in the evaluation of the canonical partition for the hydrogen atom. Using the properties of the Coulomb propagator, Blinder [4] showed that the contribution of the discrete states of hydrogen is

$$q_D = 1 + \sum_{n=2}^{\infty} e^{-E_H Z^2(1-1/n^2)/2kT} \int_0^R D_n(r)dr \tag{7}$$

and he obtained

$$q_D - 1 \approx 0.3256(ZR)^{3/2} e^{-E_H Z^2/2kT}, \tag{8}$$

where E_H is one hartree and, for the standard state, R is the radius encompassing the standard volume $N_A kT/p^0$. If the integration in (7) is carried out with the exact limiting form analytically, and the summation by Blinder's technique, the result is

$$q_D - 1 \approx 0.4553(ZR)^{3/2} e^{-E_H Z^2/2kT}. \tag{9}$$

The contribution from the continuum is, of course, unaffected by the replacement of the empirical function by the exact bound state distribution.

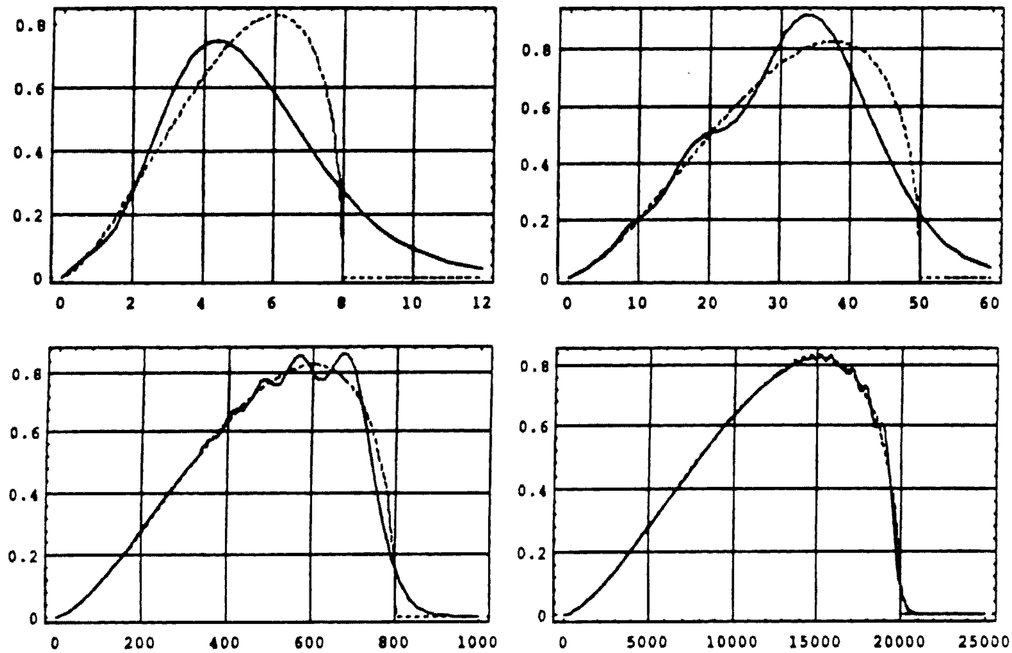

Fig. 1. Comparison of generalized radial distribution functions $D_n(r)$ with the limiting distribution (dashed curve), for $Z = 1$ and $n = 2, 5, 20, 100$. Radius in bohrs.

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References

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