Journal of Mathematical Chemistry 14 (1993) 319–324

Generalized Unsöld theorem and radial distribution function for hydrogenic orbitals

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Received 11 September 1992; revised 1 February 1993

A generalization of Unsöld's theorem is derived, giving the sum over both l and m for products of hydrogenic functions with given n. A generalized radial distribution function $D_n(r)$ is introduced and its properties discussed. As $n \to \infty$, $D_n(r)$ approaches a universal reduced form, for which an empirical representation is given.

By Unsöld's theorem [1] the sum over all m states for a shell of hydrogenlike orbitals reduces to a spherically-symmetrical function:

$$\sum_{m=-l}^{l} |\psi_{nlm}(r,\theta,\phi)|^2 = \rho_{nl}(r)\,. \tag{1}$$

For a pure Coulomb potential, the different l states for a given n are also degenerate. We present in this paper an explicit form for the sum over both l and m for hydrogenic orbitals, viz.,

$$\sum_{l=0}^{n-1} \rho_{nl}(r) = \rho_n(r)\,. \tag{2}$$

The result is not entirely new [2,3] but we will develop it here in greater detail. We encounter summations over $\rho_n(r)$ in computation of the Coulomb statistical density matrix [4,5]. The bound-state contribution is explicitly

$$\sum_{n=1}^{\infty} \rho_n(r)\ \mathrm{e}^{-\beta E_n}\,. \tag{3}$$

We note that, in recent experiments [6], hydrogen atoms have been excited by electric fields to high Rydberg states in excess of $n = 70$.

The most straightforward derivation of what we call the "generalized Unsöld

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theorem" makes use of the Coulomb Green's function. First derived in closed form by Hostler [7], the Green's function can be expressed as follows [8]:

$$G^+(\mathbf{r}_1,\mathbf{r}_2,E) = G^+(x,y,k) = -\frac{1}{\pi(x-y)}\left(\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right)g^+(x,y,k)\,, \tag{4}$$

where

$$g^+(x,y,k) = (\mathrm{i}k)^{-1}\Gamma(1-\mathrm{i}\nu)M_{\mathrm{i}\nu}(-\mathrm{i}ky)W_{\mathrm{i}\nu}(-\mathrm{i}kx)\,, \tag{5}$$

the latter function representing a pseudo one-dimensional Coulomb system. The coordinate variables x and y are defined by

$$x \equiv r_1 + r_2 + r_{12}, \quad y \equiv r_1 + r_2 - r_{12}\,. \tag{6}$$

The energy is related to the wavenumber k by

$$E = \hbar^2 k^2/2m = k^2/2 \tag{7}$$

in the atomic units: $\hbar = m = e = 1$. We also introduce the parameter

$$\nu \equiv Z/k\,. \tag{8}$$

M and W are Whittaker functions as defined by Buchholz [9]. For brevity we write $M_{\mathrm{i}\nu}$ for $M_{\mathrm{i}\nu,1/2}$ and $W_{\mathrm{i}\nu}$ for $W_{\mathrm{i}\nu,1/2}$.

We recall the spectral representation of the Green's function, running over both discrete and continuum eigenstates:

$$G(\mathbf{r}_1,\mathbf{r}_2,E) = \sum_{n,l,m}\frac{\psi_{n,l,m}(\mathbf{r}_1)\psi^*_{n,l,m}(\mathbf{r}_2)}{E-E_n} + \sum_{l,m}\int_0^\infty \frac{\psi_{k,l,m}(\mathbf{r}_1)\psi^*_{k,l,m}(\mathbf{r}_2)}{E-k^2/2}\,\mathrm{d}k \tag{9}$$

with $\mathrm{Im}\,E>0$ for G^+. The gamma function has poles at $\nu = -\mathrm{i}n, n = 1,2,\ldots$, corresponding to the discrete Coulomb spectrum $E_n = -Z^2/2n^2$. The corresponding residues of the Green's function can evidently be identified with the sum over the discrete eigenstates of a given n. We define the density function

$$\rho_n(\mathbf{r}_1,\mathbf{r}_2) = \sum_{l,m}\psi_{n,l,m}(\mathbf{r}_1)\psi^*_{n,l,m}(\mathbf{r}_2) \tag{10}$$

so that

$$\rho_n(\mathbf{r}_1,\mathbf{r}_2) = -\left(\frac{Z_n}{\pi}\right)(x-y)^{-1}\left(\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right)M_n(Z_n x)M_n(Z_n y)\,. \tag{11}$$

We have introduced the abbreviation $Z_n \equiv Z/n$. The Whittaker function for integer n are related to Laguerre functions as follows:

$$M_n(z) = \frac{z}{n}\,\mathrm{e}^{-z/2}L^{(1)}_{n-1}(z) = z\,\mathrm{e}^{-z/2}{}_1F_1(n-1;2;z)\,. \tag{12}$$

Also

$$W_n(z) = (-)^{n-1} n! M_n(z) . \tag{13}$$

This result also follows from the discrete part of the Coulomb propagator [5], but the derivation given above is more illuminating.

Note that the density functions, like the Green's function, have reduced to a function of just the two configuration variables x and y. Explicitly, the first three density functions are

$$\rho_1 = (Z^3/\pi)\ \mathrm{e}^{-Z\xi} ,$$

$$\rho_2 = (Z^3/8\pi)(1 - \tfrac{1}{2}Z\xi + \tfrac{1}{8}Z^2\eta^2)\ \mathrm{e}^{-Z\xi/2} ,$$

$$\rho_3 = \frac{Z^3}{27\pi}[1 - \tfrac{2}{3}Z\xi + \tfrac{2}{27}Z^2(\xi^2 + 2\eta^2) - \tfrac{2}{81}Z^3\xi\eta^2 + \tfrac{1}{972}Z^4\eta^4]\ \mathrm{e}^{-Z\xi/3} , \tag{14}$$

where

$$\xi \equiv (x+y)/2, \quad \eta \equiv \sqrt{xy} .$$

Application of the above formulas to hybrid atomic orbitals and open-shell computations has been suggested [8].

The analog of (11) for continuum states works out to

$$\rho_k(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{l,m} \psi_{k,l,m}(\boldsymbol{r}_1)\psi^*_{k,l,m}(\boldsymbol{r}_2)$$
$$= \frac{1}{2\pi^2}\ \mathrm{e}^{\pi\nu}|\Gamma(1-\mathrm{i}\nu)|^2(x-y)^{-1}\left(\frac{\partial}{\partial x} - \frac{\partial}{\partial y}\right)M_{\mathrm{i}\nu}(-\mathrm{i}kx)M_{\mathrm{i}\nu}(-\mathrm{i}ky) . \tag{15}$$

We now specialize $\rho_n(\boldsymbol{r}_1, \boldsymbol{r}_2)$ to the limit $\boldsymbol{r}_1 = \boldsymbol{r}_2 = \boldsymbol{r}$ or $x = y = 2r$. The result is

$$\rho_n(r) = \frac{Z_n^3}{\pi}[M_n'(2Z_nr)^2 - M_n(2Z_nr)M_n''(2Z_nr)] . \tag{16}$$

We can define the generalized radial distribution functions

$$D_n(r) \equiv 4\pi r^2 \rho_n(r) , \tag{17}$$

which are normalized according to

$$\int_0^\infty D_n(r)\mathrm{d}r = n^2 , \tag{18}$$

reflecting the orbital degeneracy of the corresponding energy level E_n.

In fig. 1 we show the radial distribution functions for n =1, 2, 5,10, 20 and 50, with $Z = 1$. As n increases, the function evidently approaches a universal reduced

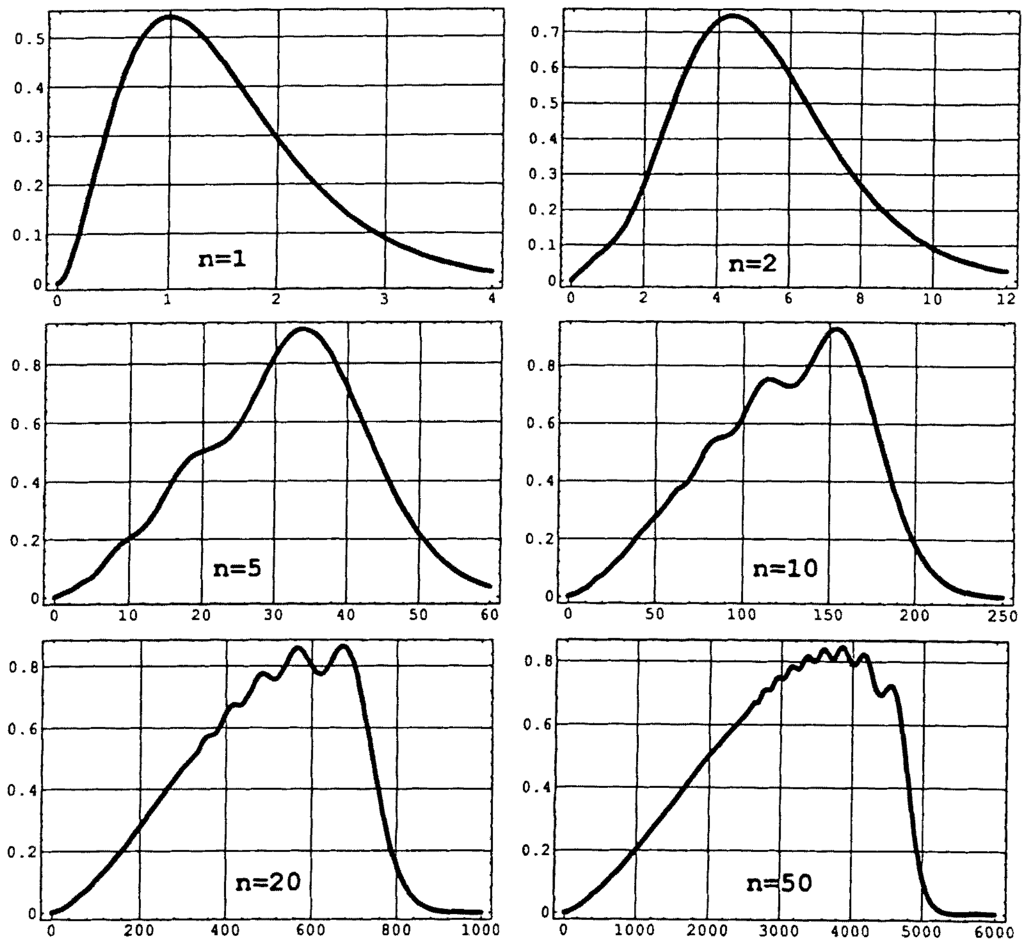

Fig. 1. Generalized radial distributions functions $D_n(r)$ for $Z = 1$, $n = 1, 2, 5, 10, 20, 50$. Radius r in bohrs.

form, apart from some small oscillations. $D_n(r)$ exhibits a maximum value ≈ 0.835 near $r \approx 1.5n^2/Z$. Remarkably, this maximum value is never exceeded for any value of n. The radial distribution functions decay rapidly beyond $r = 2n^2/Z$ and drop effectively to zero for $r \approx 2.1n^2/Z$. We were not able to derive an analytic representation for the $n \to \infty$ asymptotic form of $D_n(r)$. However, an approximate representation is suggested by the asymptotic behavior of the Whittaker function for $n \gg Zr \gg 1$, viz.,

$$M_n(2Zr/n) \sim \frac{1}{n}\sqrt{2Zr}J_1(\sqrt{8Zr}) \sim \frac{1}{\sqrt{\pi n}}(2Zr)^{1/4}\cos(\sqrt{8Zr} - 3\pi/4)\,, \tag{19}$$

which leads to

$$D_n(r) \sim \frac{Z}{\pi}\left(\frac{2Zr}{n^2}\right)^{3/2}. \tag{20}$$

This suggests the empirical representation:

$$D_n(r) \approx \frac{Z}{\pi}\rho^{3/2}(1 + a\rho + b\rho^2 + c\rho^3 + d\rho^4), \quad \rho \equiv 2Zr/n^2\,. \tag{21}$$

The best least-squares fit for $0 \leq r \leq 2.1n^2/Z$ is obtained with $a = -0.267973$, $b = 0.0863527$, $c = -0.0135544$, $d = -0.00126477$. The dashed curve in fig. 2 shows the fitted function with these parameters compared to the accurate radial distribution function for $n = 100$.

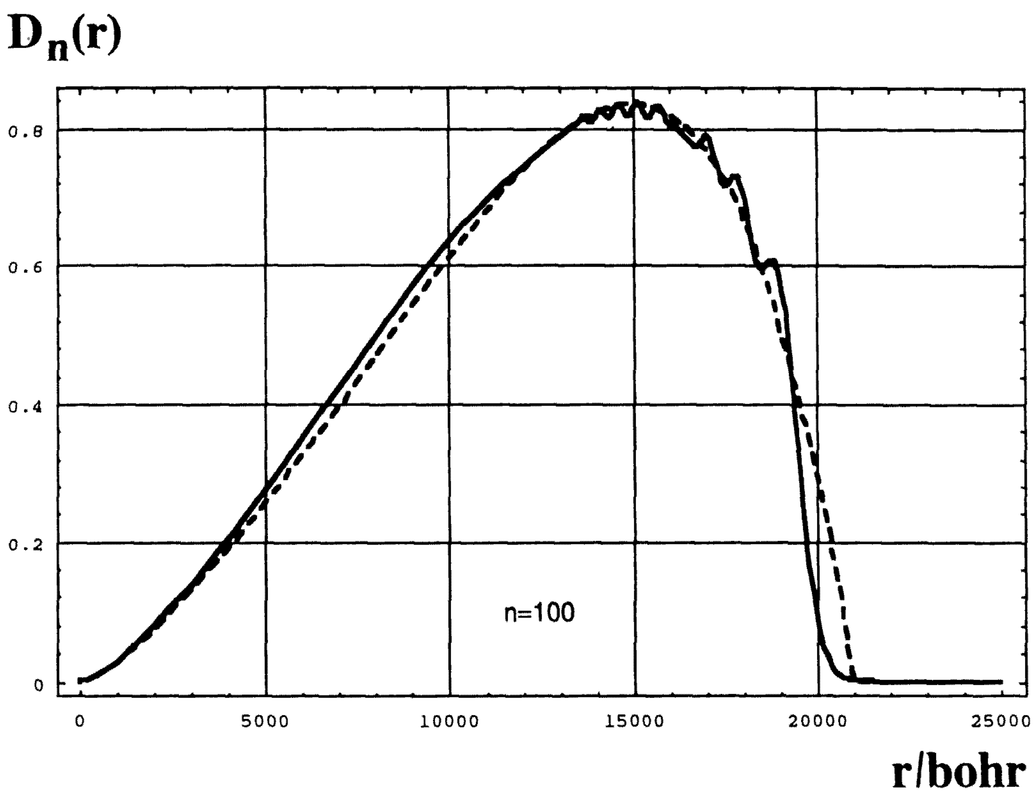

Fig. 2. Solid curve: radial distributions function for $n = 100$. Dashed curve: best fit using eq. (21).

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