

## BRIEF REPORTS

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## Thermal excitation of the H atom

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(Received 6 October 1995)

The probability of finding the electron at a point  $\vec{r}$  and at temperature  $T$  in a H atom is found by considering only the discrete states and summing over the various quantum numbers using its Fourier transform. It is shown that at high temperatures this probability is of the same form as the density of electrons in a heavy atom.

PACS number(s): 05.30.-d

One of the interesting problems in physics is the study of quantum systems at finite temperature  $T$ . The expression for the probability distribution  $P(\vec{r}, \beta)$  was given by Slater [1] as

$$P(\vec{r}, \beta) = \left[ \sum_q |\phi_q(\vec{r})|^2 \exp(-\beta E_q) \right] \times \left[ \sum_q \exp(-\beta E_q) \right]^{-1}, \quad (1)$$

where  $\phi_q$  are the exact normalized eigenfunctions of the system and  $E_q$  the corresponding eigenvalues. The parameter  $\beta = (kT)^{-1}$ , where  $k$  is the Boltzmann constant. The probability  $P(\vec{r}, \beta)$  can also be determined by the Bloch equation [2], but in the present work we would like to work directly with expression (1) as recently techniques have been developed to calculate the sums over Hermite and Laguerre polynomials.

The problem we would like to discuss here is the calculation of the probability  $P(\vec{r}, \beta)$  for the H atom. This is the probability of finding the electron at the point  $\vec{r}$  if the H atom is thermally excited. As will be shown later, unlike the one-dimensional harmonic oscillator [3], where  $P$  could be calculated in a straightforward way using the properties of Hermite polynomials, expression (1) cannot

be evaluated in a simple way for the H atom because one has to consider both the discrete and continuous states. In the present work we shall only consider the excitations that lead to bound states up to some maximum principal quantum number  $N$ . With this assumption we shall show that the probability  $P(\vec{r}, \beta)$  for high temperatures can be obtained from the density of electrons in heavy atoms [4].

Let  $\phi_{n\ell m}(\vec{r})$  denote the orthonormal set of bound states of the H atom,  $n, \ell, m$  being the usual quantum numbers. Then the probability  $P(\vec{r}, \beta)$ , given by expression (1), can be written as

$$P(\vec{r}, \beta) = \left[ \sum_{n=1}^N \sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} |\phi_{n\ell m}(\vec{r})|^2 \exp(-\beta E_n) \right] \times \left[ \sum_{n=1}^N \sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} \exp(-\beta E_n) \right]^{-1}, \quad (2)$$

$E_n$  being the bound state energies.

As shown in Ref. [4], the summation over  $m, \ell$  can be carried out by first writing the Fourier transform  $g(\vec{k}, \beta)$

$$g(\vec{k}, \beta) = \int d\vec{r} \exp(i\vec{k} \cdot \vec{r}) P(\vec{r}, \beta). \quad (3)$$

This gives the following expression for  $g(\vec{k}, \beta)$ :

$$g(\vec{k}, \beta) = \left[ \sum_{n=1}^N (n^2) \frac{(4/n^2)^{2n}}{(k^2 + 4/n^2)^{2n}} {}_2F_1 \left( -n + 1, -n + \frac{1}{2}; \frac{3}{2}; -\frac{k^2}{4/n^2} \right) \right. \\ \left. \times {}_2F_1 \left( -n + 1, -n + 1; 2; -\frac{k^2}{4/n^2} \right) \exp(\beta/2n^2) \right] \left[ \sum_{n=1}^N n^2 \exp(\beta/2n^2) \right]^{-1}, \quad (4)$$

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where  ${}_2F_1(a, b; c; x)$  is a hypergeometric function [5].

Since the hypergeometric functions in expression (4) are polynomials in  $n$ , one can calculate  $g(\vec{k}, \beta)$  at a given temperature  $T$  and invert it to find  $P(\vec{r}, \beta)$ . The most interesting result that follows from expression (4) is that for  $T \gg 1$ , the exponential functions in expression (4) go to unity and if  $N$  is sufficiently large  $g(\vec{k}, \beta)$ ,  $\beta \rightarrow 0$ , can be approximated by [4] Bessel functions, which on inversion gives  $P(\vec{r}, \beta)$ ,  $\beta \rightarrow 0$ , by the expression

$$P(\vec{r}, \beta) = \left[ \frac{4}{\pi^2 (2N^2)^3} \right] \left( \frac{r}{2N^2} \right)^{-3/2} \left( 1 - \frac{r}{2N^2} \right)^{3/2}, \quad (5)$$

$$\beta \rightarrow 0, \quad 0 \leq r \leq 2N^2.$$

The expression on the right-hand side in expression (5) is the same as the expression for the density of electrons in heavy atoms. Thus, at high temperatures  $P(\vec{r}, \beta)$  is related to the density of electrons in heavy atoms.

We would now like to make a few remarks. The first

is that at  $T = 0$ , expression (4) gives

$$g(\vec{k}, \beta) = \frac{16}{(k^2 + 4)^2}, \quad (6)$$

which is the Fourier transform of the ground state of the H atom, as it should be. Our next remark is that at high temperatures, expression (5) shows that the probability  $P$  is zero beyond  $r > 2N^2$ . This is consistent with a recent formulation of the partition function [6] of the H atom in which to get the finite results one has to use wave functions within some given volume.

Our last remark is about the effect of the inclusion of the continuum states on the expression for the probability  $P$  given by (5). It is obvious that if one uses the usual normalization for the continuum wave functions  $\delta(k - k')$ , where  $k$  is the magnitude of the momentum, one will get divergent results. The integration over a finite range of  $r$  will remove this divergence. As the continuum wave functions oscillate like spherical Bessel functions, the effect of the inclusion of the continuum on the probability will show up as small fluctuations in  $r$ .

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