Scaling Relation for the Energy Levels of a Hydrogen Atom at High Pressures

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The effect of high pressure on a hydrogen atom has frequently been simulated by enclosing the atom in an impenetrable spherical box. It is shown that for such a confined hydrogen atom placed at the centre of a spherical box a simple scaling relation exists between the energy and the radius of the confining box for 1s, 2p, 3d, and 4f levels, and another similar relation exists for 2s, 3p, and 4d levels.

Key words: Confined Hydrogen Atom; High Pressures.

1. Introduction

Since Michels et al. [1] suggested the idea of simulating the effect of pressure on an atom by enclosing it in an impenetrable spherical box, there have been quite a few investigations by a variety of techniques to calculate the energy levels of a hydrogen atom confined in a spherical box [1 - 19]. Such an atom is frequently referred to as a compressed atom or a confined atom.

Arnold Sommerfeld's contribution to a number of areas of physics are well known. He was one of the great masters of exact solutions of differential equations. He was attracted to the problem of a confined hydrogen atom because of its importance in astrophysics. Together with Welker [2] he carried out a detailed investigation on the variation of the binding energy of the 1s state of the hydrogen atom, as a function of the sphere radius r_0. The surface of the spherical box was assumed to be impenetrable, and the hydrogen atom was placed at the centre of the box. Sommerfeld and Welker [2] obtained series expansions for the ℓ =0 case, which are exact, being full generalisations from the situation where the boundary conditions apply rigorously in the non-relativistic case, namely when a node coincides with the confining boundary and the analytic solution is known. They showed that, as r_0 decreases, the binding energy diminishes and there is a critical value of the sphere radius at which the binding energy becomes zero. We shall call it the critical cage radius [20] and represent it by r_c . Sommerfeld and Welker [2] found that for the 1s state $r_c = 1.835$ (in atomic units). For $r < r_c$, the energy of the system is positive.

Sommerfeld and Welker [2] also obtained an asymptotic relation between E and r_0 for the 1s state when E is positive and very high:

$$Er_0^2 = \pi^2 = 9.8696. \qquad (1)$$

The barrier height for an impenetrable box is of course infinite. The case for finite barrier height has also been investigated [7, 14]. Some other properties of the confined hydrogen atom have also been calculated [6, 7, 14, 20]. Recently Connerade et al. [21] have explored the properties of hydrogen confined endohedrally at the geometrical centre of a spherical, attractive short-range potential. The evolution of the energy spectrum, as a function of the depth of the shell, is found to exhibit unusual level crossings and degeneracies resulting in avoided crossings and a new phenomenon of 'mirror collapse', where the localized states switch places.

In the present paper we shall show that for the hydrogen atom, placed at the center of an impenetrable spherical box, a simple scaling relation exists between the energy and the radius of the confining box for 1s, 2p, 3d, and 4f levels ($n = \ell + 1$), and another similar relation for 2s, 3p, and 4d levels ($n = \ell + 2$).

We shall use atomic units such that the unit of distance is the Bohr radius a_0, and the unit of energy is the Rydberg constant. We shall represent the energy

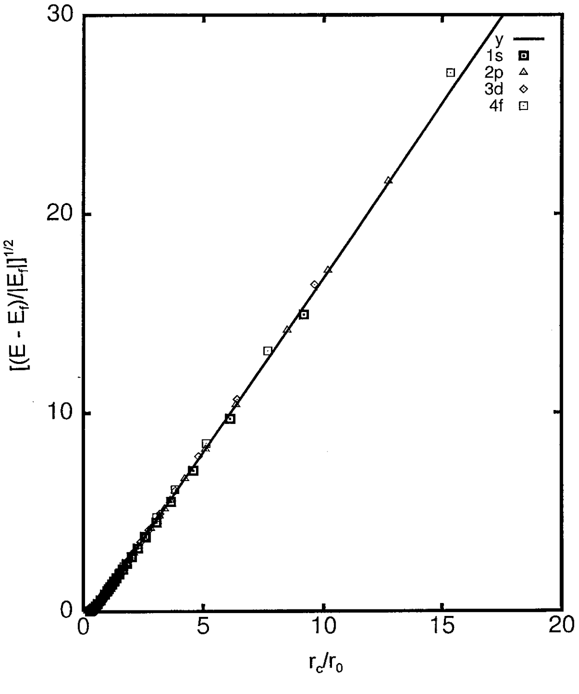

Fig. 1. $[(E - E_f)/|E_f|]^{1/2}$ versus r_c/r_0 for 1s, 2p, 3d, and 4f levels of hydrogen. The straight line represents (4).

of a level for the confined atom by E, and the energy of the same level for the free atom by E_f. The radius of the confining box (or cage) shall be represented by r_0. We shall also find it sometimes convenient to use the variables

$$y = [(E - E_f)/|E_f|]^{1/2}, \tag{2}$$

$$x = r_c/r_0. \tag{3}$$

2. Scaling Relation

We have found that, if one plots $[(E - E_f)/|E_f|]^{1/2}$ versus r_c/r_0 for 1s, 2p, 3d, and 4f levels of hydrogen, the resulting distribution of points can be represented by a smooth curve. Such a plot is shown in Figure 1. The data for the 1s, 2p, and 3d levels are from [18] and [20]. For the 4f level, fresh calculations for exact values of the energy were carried out by the author. It will also be noticed from Fig. 1 that for a large part this relationship can be represented by a linear relation. The linearity extends down to $x \simeq 0.7$. A least-squares treatment yields the relation

$$y = 1.7520\,x - 0.7535 \tag{4}$$

and is shown in Figure 1.

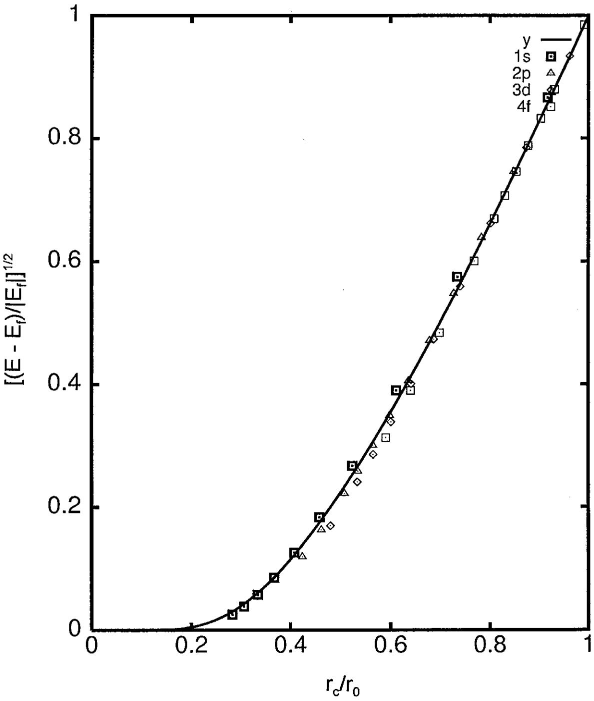

Fig. 2. $[(E - E_f)/|E_f|]^{1/2}$ versus r_c/r_0 for 1s, 2p, 3d, and 4f levels for $x \leq 1$. The curve represents (5).

The region for $x \leq 1$ (negative energy states) is shown on an enlarged scale in Figure 2. The departure from linearity is clearly seen. The distribution of points in Fig. 2 can be represented by an empirical equation of the form

$$y = \frac{2.497}{\exp(1.252/x) - 1} \tag{5}$$

and is shown by the solid line curve in Figure 2. We may note that (5) is not valid for $x > 1$.

Though we have demonstrated the existence of the scaling relation only for the 1s, 2p, 3d, and 4f states, it would be a reasonable extrapolation to expect that it would hold for all $n = \ell + 1$ type of levels.

When x is very large, the constant term on the right hand side of (4) can be neglected, and similarly E_f can be neglected in comparison with E in the numerator of the left hand side. Then (4) in the limiting case leads to

$$\frac{E}{E_f}\frac{r_0^2}{r_c^2} = 3.0695 \tag{6}$$

For the 1s state, (6) reduces to

$$Er_0^2 = 10.338. \tag{7}$$

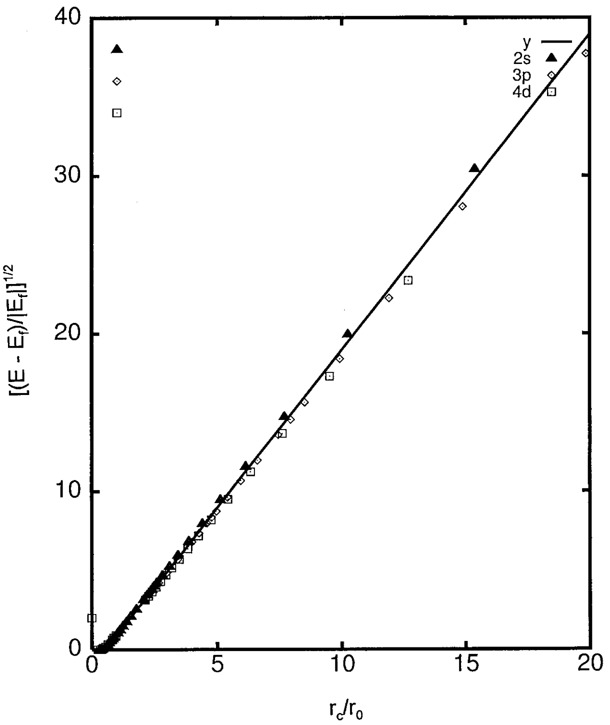

Fig. 3. $[(E - E_\mathrm{f})/|E_\mathrm{f}|]^{1/2}$ versus r_c/r_0 for 2s, 3p, and 4d states. The straight line represents (9).

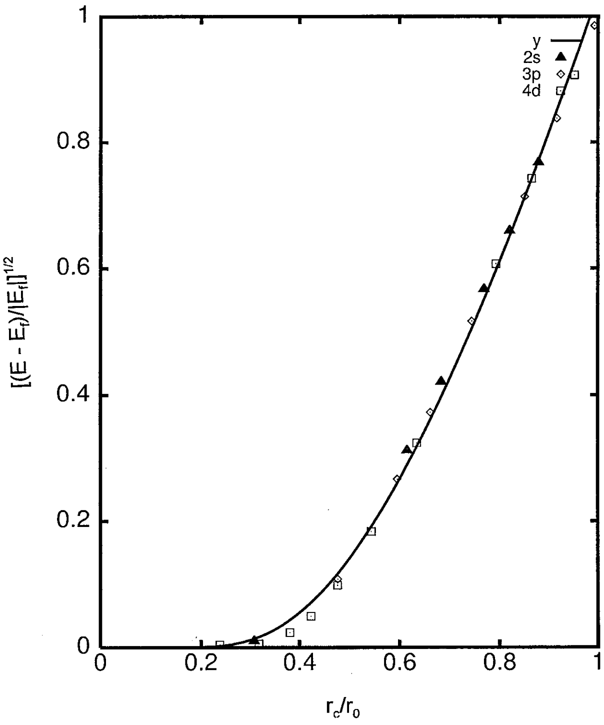

Fig. 4. $[(E - E_\mathrm{f})/|E_\mathrm{f}|]^{1/2}$ versus r_c/r_0 for 2s, 3p, and 4d states for $x \leq 1$. The curve represents (10).

We find that the empirical value of Er_0^2 is quite close to the theoretical value of 9.8696 obtained by Sommerfeld and Welker [2]. We may generalize the result of [2] in an approximate way, as follows for the $n = l + 1$ type of levels:

$$\frac{E}{E_\mathrm{f}}\frac{r_0^2}{r_\mathrm{c}^2} = 2.9304. \tag{8}$$

A plot of y versus x for 2s, 3p, and 4d states is shown in Figure 3. For these levels, fresh calculations for exact values of the energy were carried out by the author. r_c values are from [20]. Here again it will be noticed that for a large part this relationship can be represented by a linear relation. In this case also the linearity extends down to $x \simeq 0.7$. A least-squares treatment leads to the relation

$$y = 2.0004\,x - 1.0399 \tag{9}$$

and is shown in Figure 3.

The region for $x \leq 1$ (negative energy states) for 2s, 3p, and 4d states is shown on an enlarged scale in Figure 4. In this case also the distribution of points can be represented by an empirical equation of the same form as (4):

$$y = \frac{5.566}{\exp(1.851/x) - 1}, \tag{10}$$

and is shown by the solid line curve in Figure 4. We may note that (10) is not applicable for $x > 1$.

The pressure P exerted on the wall of the box is given by

$$P = -\frac{1}{4\pi r_0^2}\frac{\mathrm{d}E}{\mathrm{d}r_0} \tag{11}$$

which, in conjunction with (4) or (9), gives

$$P = a_1/r_0 - a_2, \tag{12}$$

where a_1 and a_2 are constants which depend on the level. Thus the pressure varies linearly with $1/r_0$.

The relations presented in this paper can be used to calculate the energy for any given value of r_0 for the following levels: 1s, 2p, 3d, 4f, 2s, 3p, and 4d. The relations are, of course, not exact, as the spread of points indicates, but are a very good first approximation and are of the practical use for simplifying the calculation of partition function and other thermodynamic properties of hydrogen at high pressures. It is highly likely that similar relations hold for other levels also.

We have already noted that the importance of r_c was first recognized by Sommerfeld and Welker [2]. The critical cage radius r_c of hydrogen is relevant in the calculation of the partition function of atomic hydrogen and also in studies concerning pressure ionization of ground and excited states of hydrogen. In the calculation of the partition function one must truncate the sum at a suitable point. One reasonable criterion for this purpose is to take the sum upto that level for which r_c is equal to half of the mean distance between atoms. The present investigation has revealed a new significance of r_c in the context of a confined hydrogen atom, that is it gives rise to certain scaling relations.

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