Spectrum of helium at high pressures

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Abstract. The effect of high pressures on an atom is frequently simulated by enclosing the atom in an impenetrable spherical box. The spectrum of such a confined helium atom placed at the centre of a spherical box is investigated. A model potential is used to calculate the energies of twelve excited states and thereby the transition wavelengths for a range of values of the radius of the confining sphere. Applications of results are discussed.

PACS. 32.30.-r Atomic spectra – 32.70.Jz Line shapes, widths, and shifts – 31.70.Dk Environmental and solvent effects – 52.25.Os Emission, absorption, and scattering of electromagnetic radiation

1 Introduction

In recent years there has been a great deal of interest in the properties of helium at high pressures. The understanding of the physical properties of helium under high pressures is a crucial problem in dense matter physics, as much from a fundamental viewpoint as for physical and astrophysical applications. Further, the properties of helium atoms confined to move in restricted geometry have been of considerable interest during the last several decades.

Michels *et al.* [1] first suggested the idea of simulating the effect of pressure on an atom by enclosing it in an impenetrable spherical box. Over the years there have been a number of investigations by a variety of techniques to calculate the energy levels and other properties of a hydrogen atom confined in a spherical box [1–11]. Both cases have been considered, that is the barrier height being infinite and finite. Such an atom is frequently referred to as a compressed atom or a confined atom. The confined helium atom has, however, received much less attention because of more complicated calculations. A few studies [7,12–15] have been published, but these are all on the ground state.

The excited states of helium arise when one of the 1s electrons is raised to a higher level. In the present paper we investigate the effect of confinement on some of the lower lying excited states and the resulting optical spectrum from transitions between these states. Such an investigation is of interest to at least two areas of physics and also in astrophysics. We shall discuss these later in this paper. Unless otherwise stated, throughout this paper we shall use atomic units such that the unit of length is the Bohr radius a_0, and the unit of energy is Rydberg.

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2 Theory

Atomic model potentials are often used for many atomic problems [16–19]. Here also we shall adopt an independent electron model which is combined with a model potential to represent the helium atom. This approach has been found to be quite successful for representing the excited states of the helium atom (but not the ground state). We represent the interaction of the active electron with the He$^+$ core by the following model potential.

$$V(r) = -\frac{1}{r} + \frac{1}{r}(1 + \beta r)e^{-2\beta r} \qquad (1)$$

where β is a parameter.

This potential or it's two parameter version has been used for helium (or helium-like ions) in several atomic problems [20–24]. This potential has a theoretical basis. Gerry and Laub [25] have studied this potential by the dynamical-group method. Sever and Tezcan [26] and Varshni [27] have studied the bound states of a two-parameter version of potential (3). Several other model potentials for helium exist in the literature [28–37].

In this paper we shall consider twelve excited states which are identified in Table 1. The wavelengths that arise from transitions between these levels are shown in Table 2.

The Schrödinger equation for potential (1) is not analytically solvable. It is not possible to achieve high degree of accuracy for excited states from approximation methods like the variational method or the WKB method. Further the variational method gives only an upper bound to the energy, and the values obtained for excited states can be liable to large uncertainties. Hence it was thought best to carry out the necessary calculations by direct numerical integration of the Schrödinger equation, because this

Table 1. Values of α and β for the twelve states.

Configuration	Term	α	β
$1s2s$	^{1}S	1.0	2.601
$1s3s$	^{1}S	1.0	2.668
$1s4s$	^{1}S	1.0	2.688
$1s2p$	^{1}P	0.9934	2.601
$1s3p$	^{1}P	0.9949	2.668
$1s4p$	^{1}P	0.9960	2.688
$1s2s$	^{3}S	1.0	0.9156
$1s3s$	^{3}S	1.0	0.9286
$1s4s$	^{3}S	1.0	0.9331
$1s2p$	^{3}P	0.9849	0.9156
$1s3p$	^{3}P	0.9910	0.9286
$1s4p$	^{3}P	0.9935	0.9331

Table 2. Wavelengths (in angstroms) for singlet and triplet transitions for a free atom.

Transition	Wavelength
$1s2s$ ^{1}S–$1s3p$ ^{1}P	5 015.7
$1s2s$ ^{1}S–$1s4p$ ^{1}P	3 964.7
$1s2s$ ^{1}P–$1s3s$ ^{1}S	7 281.4
$1s2s$ ^{1}P–$1s4s$ ^{1}S	5 047.7
$1s2s$ ^{3}S–$1s3p$ ^{3}P	3 888.6
$1s2s$ ^{3}S–$1s4p$ ^{3}P	3 187.7
$1s2s$ ^{3}P–$1s3s$ ^{3}S	7 065.2
$1s2s$ ^{3}P–$1s4s$ ^{3}S	4 713.2

Table 3. Variation of the wavelength with r_0 for singlets. All wavelengths are in angstroms.

r_0	$\lambda = 5015.7$	$\lambda = 3964.7$	$\lambda = 7281.4$	$\lambda = 5047.7$
30	5 011.0	3 789.7	7 275.7	4 803.9
32	5 013.8	3 848.6	7 279.2	4 890.9
34	5 014.9	3 889.2	7 280.6	4 949.1
36	5 015.4	3 916.5	7 281.1	4 987.1
38	5 015.6	3 934.6	7 281.3	5 011.3
40	5 015.6	3 946.3	7 281.4	5 026.4
42	5 015.7	3 953.7	7 281.4	5 035.5
44	5 015.7	3 958.3	7 281.4	5 040.9
46	5 015.7	3 961.0	7 281.4	5 044.0
48	5 015.7	3 962.6	7 281.4	5 045.7
50	5 015.7	3 963.6	7 281.4	5 046.7

Table 4. Variation of the wavelength with r_0 for triplets. All wavelengths are in angstroms.

r_0	$\lambda = 3888.6$	$\lambda = 3187.7$	$\lambda = 7065.2$	$\lambda = 4713.2$
30	3 887.0	3 095.2	7 063.7	4 575.3
32	3 888.0	3 128.0	7 064.7	4 629.4
34	3 888.4	3 149.9	7 065.0	4 663.6
36	3 888.5	3 164.3	7 065.2	4 684.5
38	3 888.6	3 173.5	7 065.2	4 697.1
40	3 888.6	3 179.3	7 065.2	4 704.4
42	3 888.6	3 182.8	7 065.2	4 708.5
44	3 888.6	3 184.9	7 065.2	4 710.7
46	3 888.6	3 186.2	7 065.2	4 712.0
48	3 888.6	3 186.9	7 065.2	4 712.6
50	3 888.6	3 187.3	7 065.2	4 712.9

method, if properly implemented and fully tested, can give eigenenergies of high accuracy. The eigenenergies for potential (1) were obtained by the numerical integration of the Schrödinger equation using Numerov's method and the logarithmic mesh.

In potential (1), the parameter β has different values for singlet and triplet states. The parameter β was optimised so that the eigenvalues reproduce as well as possible the experimental values of ^{1}S and ^{3}S levels. For the singlet levels, β was determined to be 2.62 and for the triplet levels, 0.917. It was found that these values of β are able to give energy values for all the levels listed in Table 1 which are in reasonable agreement (2 or 3 significant figures) with the experimental values. However, to obtain a closer agreement, the value of β has to be given a slightly different value for each ^{1}S and ^{3}S states. For a given state, the energy by potential (1) was obtained for different values of the parameter β until 4 or 5 significant figure agreement with the experimental energy value was obtained. For ^{1}P and ^{3}P states, to obtain a similar agreement, it becomes necessary to introduce a second parameter, α. Thus equation (1) becomes

$$V(r) = -\frac{\alpha}{r} + \frac{1}{r}(1 + \beta r)\mathrm{e}^{-2\beta r}. \qquad (2)$$

For a given state, the value of β was taken to be the same as that of the corresponding S state and α was varied. The values of α and β thus obtained are given in Table 1.

3 Results and discussion

We shall consider a helium atom placed at the center of a impenetrable spherical box with a radius r_0. Again, the numerical integration of the Schrödinger equation was employed to calculate energy values of these twelve states for a large number of values of r_0. The wavelengths for transitions between singlet levels for a range of values of r_0 are given in Table 3 and those for triplet levels in Table 4. For lower values of r_0, as an example, the results for the $1s2p^1$P state are shown in Figure 1. It will be noticed in Tables 3 and 4 that in all cases the wavelengths decrease as r_0 is reduced, in other words a blue shift. In addition to this shift, the spectral lines will be broadened due to Doppler and pressure broadening [38–40].

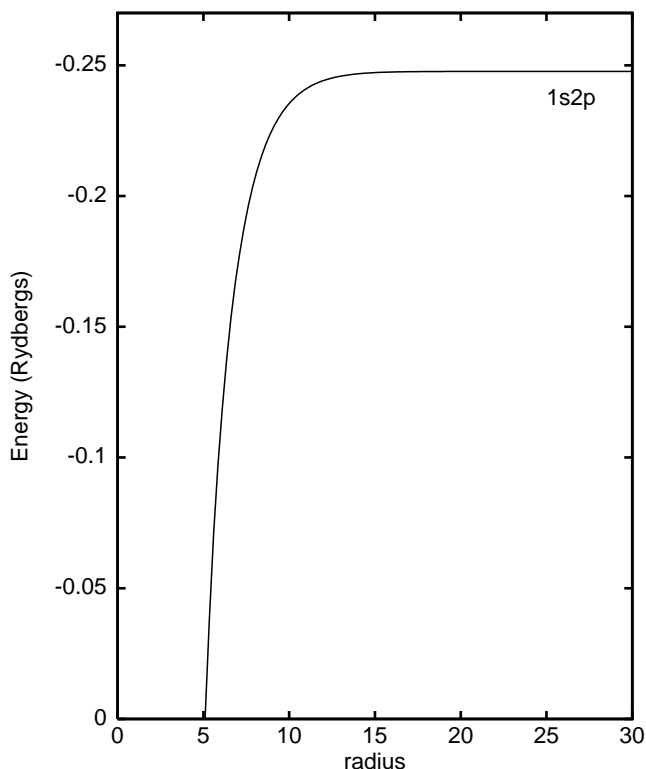Next we consider the applicability of these results to a number of areas.

Fig. 1. Variation of the energy of the $1s2p\,^1$P state with the radius r_0 (atomic units).
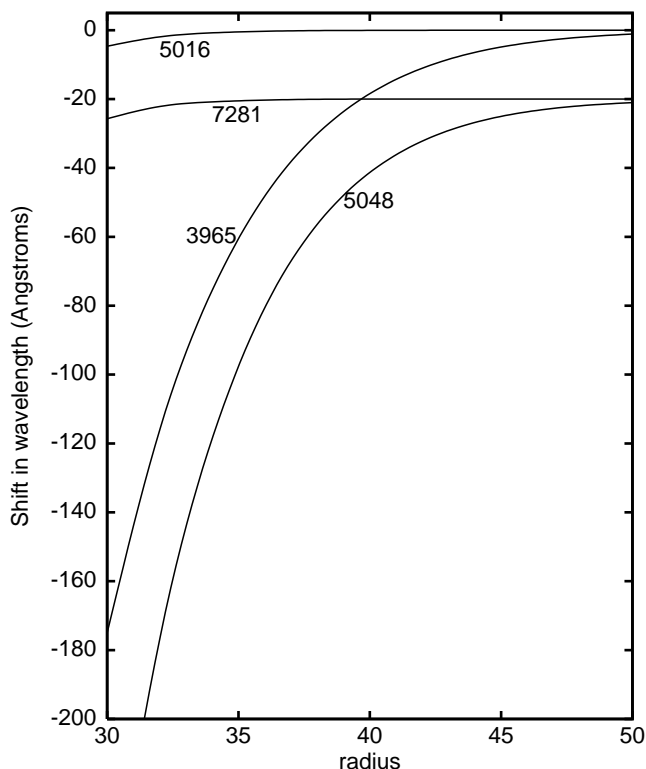

Fig. 2. Shift of singlet lines from the free atom value as a function of the radius r_0 (atomic units).

(a) Bubbles of helium have been implanted in a variety of materials, *e.g.*, metals [41–45], Vycor porous glass [46,47], aerogels [47,48] etc. The physical state of helium in these bubbles has to be inferred by indirect means.

Lucas *et al.* [43] have used three techniques, namely Absorption, Electron Energy Loss and Fluorescence Spectroscopies to study thin film samples of helium/aluminum composite containing a few atomic percent of helium. The spectral range between 5 and 30 eV was explored. Between 20 and 25 eV, by absorption spectroscopy they found detection of the helium resonance line strongly broadened and shifted towards higher energies.

Rohlfing [45] has performed vacuum ultraviolet absorption and electron energy loss spectroscopy on helium gas bubbles implanted in thin aluminium films. The resulting spectra have been interpreted in terms of blue-shifted atomic transitions. Broad spectral features in the region of 21–25 eV were observed experimentally and have been interpreted as blue shifts of up to 3.3 eV in the He atomic transition of 21.21 eV. He found that Taylor's [49] theoretical result of a maximum shift of 1.5 eV, based on a model of helium atom clusters, is unable to explain it.

Let us now see how these results can be explained in the framework of the confined helium atom model. The He atomic transition of 21.21 eV arises from level $1s2p\,^1$P to the ground state $1s^2$. Our results show that the $1s2p\,^1$P level decreases in energy (Fig. 1), ultimately disappearing at $r_0 \simeq 5.1$. Ludena's [12] calculations based on SCF show that there is negligible change in the energy of the ground state $1s^2$ at this value of r_0 from the free atom value.
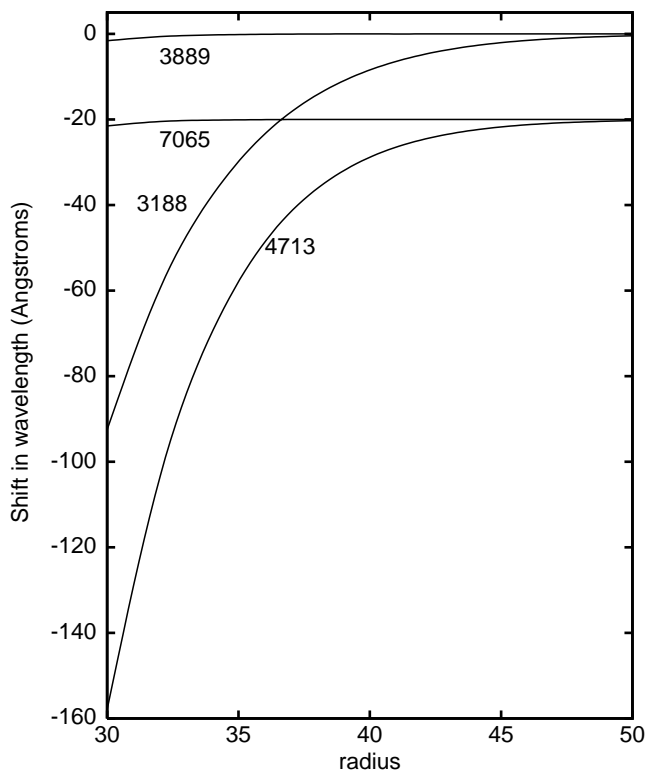

Fig. 3. Shift of triplet lines from the free atom value as a function of the radius r_0 (atomic units).

This means that as the number density of helium atoms will increase the line will be shifted to shorter wavelengths and practically all the change will be due to the shift of the upper level. The transition energy at $r_0 = 5.1$ will be 24.58 eV. Actual spectral lines will of course stop a little before this limit. The bubbles are of different sizes and having different number density of helium atoms. Thus we expect a spectral band between 21.21 and 24.58 eV. As noted earlier, Rohlfing's [45] observed broad spectral features in the region of 21.21 to 24.5 eV. The naturalness of the explanation and the good numerical agreement indicates that very likely this is the correct explanation of the experimental observations.

The model employed here represents only approximately a realistic system containing helium atoms under high pressure, and the exact value of r_0 at which $1s2p^1\mathrm{P}$ level will disappear may be somewhat different from 5.1, being probably somewhat larger. But it is obvious that the exact value of r_0 is not vital for the explanation.

(b) High-pressure helium plasmas. Some optical experiments have been carried out on high-pressure helium plasma [50,51], but no accurate data on the shift of lines that we have considered are available. If the shift of these spectral lines could be accurately measured, the results of the present paper could provide a quantitative diagnostic for plasma density.

(c) Astrophysics. There are certain white dwarf stars known as helium white dwarfs. As the name indicates, the spectra of these stars shows helium lines. Some of these white dwarfs have very high-pressure atmospheres. Further some of them show a rather puzzling spectrum, in which the lines have not been satisfactorily identified. The present investigation may be of help in this matter. We shall consider it in detail separately.

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