Atomic swelling upon compression

V K Dolmatov and J L King[1]

Department of Physics and Earth Science, University of North Alabama, Florence, AL 35632, USA

E-mail: vkdolmatov@una.edu

Abstract

The hydrogen atom under the pressure of a spherical penetrable confinement potential of a decreasing radius r_0 is explored, as a case study. A counter-intuitive effect of atomic swelling, rather than shrinking, with decreasing r_0 is unraveled when r_0 reaches, and remains smaller than, a certain critical value. Upon swelling, the size of the atom is shown to increase by an order of magnitude, or more, compared to the size of the free atom. Changes of photoabsorption properties of the hydrogen atom under said confinement are uncovered and demonstrated.

(Some figures may appear in colour only in the online journal)

Modifications in the structure and spectra of atoms confined in cages whose sizes are commensurable with atomic sizes have been probed by researchers since the early works of Michels *et al* [1] and Sommerfeld and Welker [2] devoted to hydrogen centrally confined in an impenetrable square-well of adjustable radius in order to simulate pressure. To date, numerous aspects of the structure and spectra of atoms under various kinds of confinements have been attacked from many different angles by research teams world-wide. This has resulted in a huge array of unravelled effects and data being accumulated in a large number of publications, see reviews [3–5] as well as numerous review papers in [6, 7] (and references therein). There, one finds a wealth of information on properties of single-electron, two-electron and many-electron atoms confined by impenetrable spherical, spheroidal, as well as open boundary potentials (e.g., see review papers in [6] by Aquino, p 123; Laughlin, p 203; Cruz, p 255; Garza and Vargas, p 241), oscillator potentials (e.g., [6, p 1]), potentials limited by conoidal boundaries ([6, p 79]), Debye potentials (Sil, Canuto and Mukherjee [7]), fullerene-cage potentials ([7, p 13], [7, p 69]), etc. All these activities speak to the importance of the subject. This is because confined atoms behave differently than free atoms in ways which provide insight into various interesting problems of interdisciplinary importance. To list a few, the latter could be associated with atoms trapped in hollow cavities of solids, zeolites, fullerenes, helium droplets formed in walls of nuclear reactors, atoms/ions placed in a plasma environment, etc. Furthermore, by suitably tailoring

the confinement parameters, novel atomic properties can be designed in a controllable manner, thereby opening up new technological possibilities for confined atoms.

The aim of this paper is to demonstrate that upon compression of an atom by a suitably tailored repulsive confining spherical potential $U_c(r)$ of a finite height and thickness, the atom can be transformed into an exotic atom of a large size and distinct spectra. It is found that upon decreasing the radius of the confining potential (thereby increasing the pressure on a confined atom) below a certain critical value r_c, the atom stops behaving in the conventional manner. Instead, the atom suddenly swells rather than keeps shrinking in size. This effect is termed *atomic swelling*. It is the ultimate aim of this paper to demonstrate and interpret atomic swelling, as well as to explore trends which might occur in photoabsorption spectra of confined atoms upon atomic swelling. The hydrogen atom is chosen as a touchstone for such a study. Atomic units (au) are used throughout the paper unless otherwise specified.

For confined hydrogen, radial wavefunctions $P_{n(\epsilon)\ell}(r)$ and energies $E_{n(\epsilon)\ell}$ of discrete states $n\ell$ or continuum spectrum $\epsilon\ell$, in the presence of a spherical confinement modelled by a confining potential $U_c(r)$, are determined by a radial Schrödinger equation

$$-\frac{1}{2}\frac{\mathrm{d}^2 P_{n(\epsilon)\ell}}{\mathrm{d}r^2} + \left[\frac{-1}{r} + \frac{\ell(\ell+1)}{2r^2} + U_c(r)\right]P_{n(\epsilon)\ell}(r) = E_{n(\epsilon)\ell}P_{n(\epsilon)\ell}(r). \quad (1)$$

First, as a guiding step in understanding which aspects of a confined/compressed hydrogen atom (labelled H@U_c) are most unusual, $U_c(r)$ is approximated by a square-well potential

---

[1] Present address: Department of Physics, Auburn University, Auburn, AL 36849, USA.
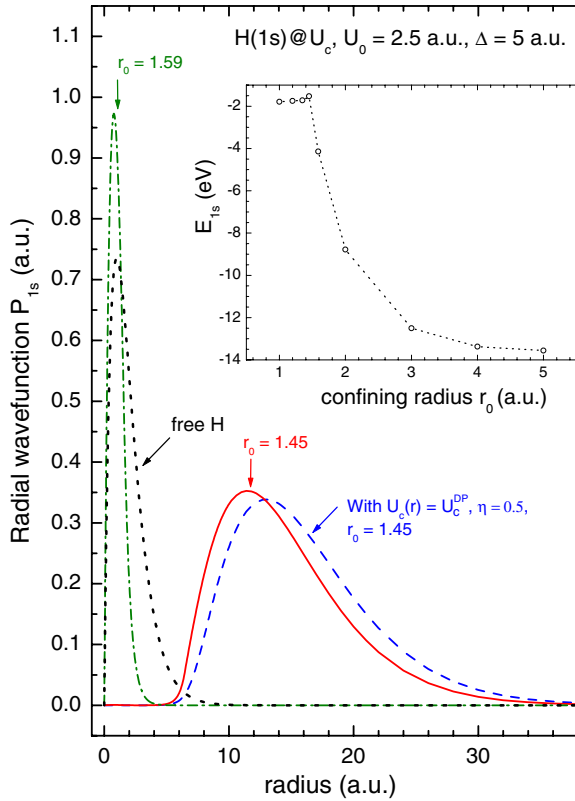
Figure 1. The 1s radial wavefunction $P_{1s}(r)$ of hydrogen confined by a square-well potential with $U_0 = 2.5$ au and $\Delta = 5$ au calculated for $r_0 = 1.59$ and 1.45 au, as marked. Also plotted are calculated data obtained with the use of a diffuse confining potential $U^{DP}(r)$ with $\eta = 0.5$, as well as data for free hydrogen, as marked. Inset: the 1s electron energy versus the confining radius r_0 of the square-well potential.

of certain adjustable inner radius r_0, height $U_0 > 0$ and thickness Δ, as in [8]:

$$U_c(r) = \begin{cases} U_0 > 0, & \text{if } r_0 \leqslant r \leqslant r_0 + \Delta \\ 0 & \text{otherwise.} \end{cases} \qquad (2)$$

However, the square-well with infinitely sharp boundaries might induce some artefacts in the structure and spectra of H@$U_c(r)$. Therefore, a trial study where the square-well potential is replaced by a potential with diffuse boundaries (to be labelled as $U_c^{DP}(r)$) is conducted in this paper as well. For this, $U_c^{DP}(r)$ is represented by the sum of two repulsive Woods–Saxon potentials:

$$
U_c^{DP}(r) = \left. \frac{2U_0}{1 + \exp\left(\frac{r_0 - r}{\eta}\right)} \right|_{r \leqslant r_0 + \frac{1}{2}\Delta}
$$
$$
+ \left. \frac{2U_0}{1 + \exp\left(\frac{r - r_0 - \Delta}{\eta}\right)} \right|_{r > r_0 + \frac{1}{2}\Delta}. \qquad (3)
$$

Here, η is the diffuseness parameter, and r_0, U_0 and Δ are the same as the parameters of the square-well potential (2). In this paper, the U_0, Δ and η parameter values are arbitrarily chosen to be $U_0 = 2.5$, $\Delta = 5$ and $\eta = 0.5$, just as a case study.

One of the key results of the study—atomic swelling upon compression—is demonstrated by figure 1 for the 1s ground-state of hydrogen under compression. First, one can

see that the $P_{1s}(r)$ wavefunction of H@U_c contracts into the inner region of space as r_0 is decreased from $r_0 = \infty$ (free hydrogen) to $r_0 = 1.59$. The energy E_{1s}, in turn, increases (less binding) from $E_{1s} \approx -13.6$ eV for free hydrogen to $E_{1s} \approx -4.14$ eV for H@U_c at $r_0 = 1.59$. Thus far, both $P_{1s}(r)$ and E_{1s} behave in the conventional manner. However, at smaller r_0, specifically, at $r_0 = 1.45$ versus $r_0 = 1.59$, the 1s orbital suddenly expands into an outer region in space, where it becomes noticeably diffuse and peaks at $r \approx 11.5$ or $r \approx 13$, depending on whether the atom is confined by the square-well or diffuse potential, respectively. The implication is that under the increased pressure, when r_0 reaches the value of $r_0 = 1.45$, the atom suddenly swells strongly, rather than keeps shrinking in size—the effect referred to as *atomic swelling* in this paper. At $r_0 = 1.45$, due to spectacular atomic swelling, the atomic size becomes more than an order of magnitude larger than the size of the free atom. A trial calculation showed that a further decrease of r_0 barely affects $P_{1s}(r)$ and E_{1s}; both of them remain practically unchanged at $r_0 \leqslant 1.45$. This is because, at $r_0 \leqslant 1.45$, almost all of the 1s electron density concentrates outside of the confining potential. Therefore, decreasing r_0 below $r_0 = 1.45$ cannot exert any more pressure on the atom. Hence, both $P_{1s}(r)$ and E_{1s} change little for all $r_0 \leqslant 1.45$. Next, the $P_{1s}(r)$ function, calculated with the use of the square-well potential, is almost the same as $P_{1s}(r)$ found with the help of the diffuse confining potential $U_c^{DP}(r)$. This is clearly seen in figure 1. One can conclude that, first, atomic swelling is not an artefact caused by the infinitely sharp boundaries of the square-well potential and, second, the phenomenon is somewhat insensitive to the shape of a penetrable confining potential. For this reason, all other calculated results presented in this paper were obtained by employing only the square-well confining potential in calculations, for the sake of simplicity.

Interestingly, the effect of atomic swelling is opposite to another counter-intuitive effect of *orbital compression* by *attractive confinement* which was revealed earlier in work [9]. Finally, note, the attempt to calculate $P_{1s}(r)$ and E_{1s} between $1.45 < r_0 < 1.59$ failed; a reason for this is explained later in the paper.

The physics behind atomic swelling becomes clear when one explores figure 2. There, the effective potential $U_{1s}^{\text{eff}}(r) = -\frac{1}{r} + U_c(r)$ 'seen' by the 1s electron in the H@U_c atom is depicted. One can see that adding the confining potential to the atomic potential makes $U_{1s}^{\text{eff}}(r)$ consist of two wells, namely, a short-range inner well and a shallow long-range outer well. As long as the confining radius r_0 is such that the inner short-range is more binding than the outer well, the 1s electron remains in the inner well. There, the atom behaves 'normally', i.e. its size is shrinking and the E_{1s} energy rising with decreasing r_0. However, when r_0 reaches some critical value r_c, the inner well becomes less binding for all $r_0 \leqslant r_c$, and so the binding of the electron alters in favour of the long-range outer well. As a result, atomic swelling into the outer well takes place for all $r_0 \leqslant r_c$. For example, as was shown above, atomic swelling of the ground-state hydrogen atom takes place at $r_0 \leqslant 1.45$.
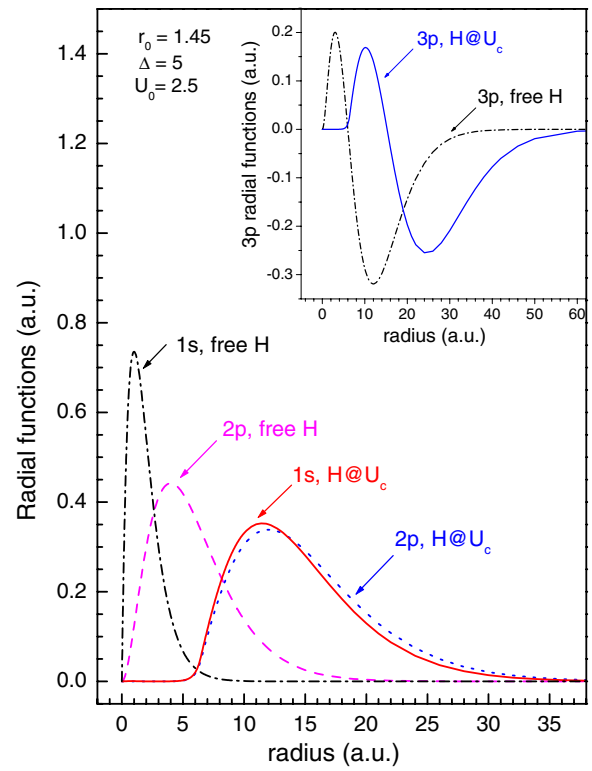
Note, the double-well potential naturally occurs in d- and f-series of free atoms. It leads to the effect known as

J. Phys. B: At. Mol. Opt. Phys. **45** (2012) 225003

V K Dolmatov and J L King
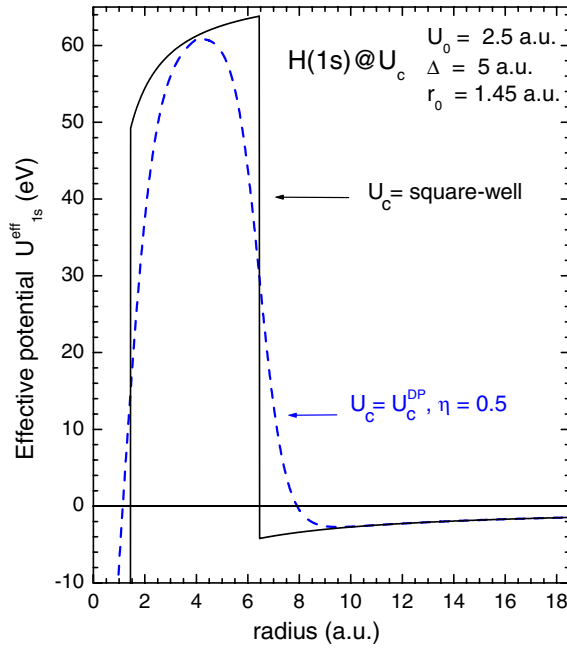
Figure 2. The effective potential $U_{1s}^{eff}(r) = -\frac{1}{r} + U_c(r)$ 'seen' by the 1s electron in the H@U_c atom when the confining potential U_c is approximated by a square-well potential with $U_0 = 2.5$, $r_0 = 1.45$ and $\Delta = 5$ au (solid line), or diffuse potential U_c^{DP} with $\eta = 0.5$, as marked.
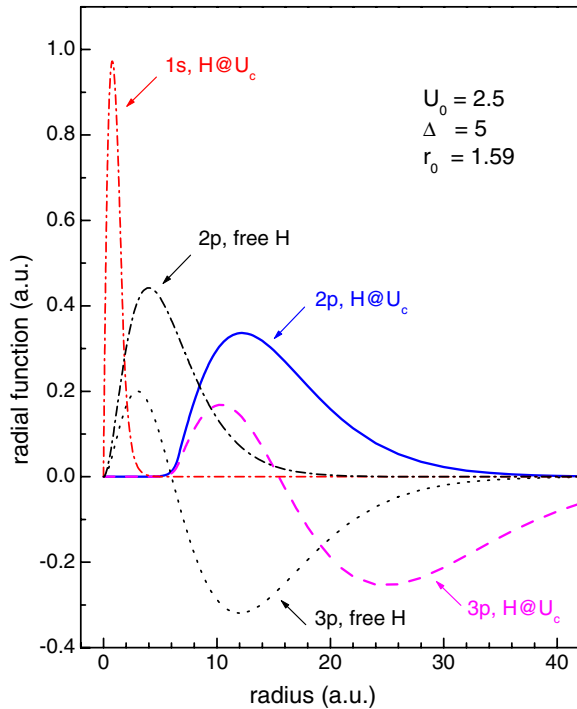

Figure 3. Radial functions $P_{1s}(r)$, $P_{2p}(r)$ and $P_{3p}(r)$ of free hydrogen and hydrogen confined by the square-well potential U_c with $U_0 = 2.5$, $r_0 = 1.45$ and $\Delta = 5$ au, as marked.

orbital collapse. The latter results in a sudden shrinking of the orbital size when the inner well becomes more binding (a thorough review of the topic was given by Connerade [10]). Orbital collapse is due to the centrifugal term in the effective atomic potential. It affects only states with $\ell \neq 0$, in contrast to atomic swelling that affects states with $\ell \geqslant 0$, as the present study shows. Both phenomena, however, are clearly similar in spirit. Furthermore, even closer in spirit, but opposite in intention and outcome, was the study performed in [11, 12]. There, double-well potential atoms, in which one of the electrons was originally bound by an outer long-range well (such, e.g., as an excited 3d* electron in Cr($3p^5 3d^5 4s^1 3d^*$, ^{7}P)), were placed inside a spherical potential of a finite or infinite potential height U_0, *infinite* thickness $\Delta \to \infty$ and adjustable confining radius r_0. It was shown that placing an outer wall of the confining potential (by properly adjusting r_0) in the domain of the outer long-range well turns the latter into a short-range well of a lesser binding capability. As a result, the competition between the inner and outer wells alters in favour of the inner well, thereby leading to 3d* orbital collapse into the inner well. In the present study, on the contrary, due to *finite* Δ, the outer well is artificially *created* and its binding capability enhances with decreasing r_0 (the well becomes deeper and wider) whereas the *inner* well loses the binding strength (the well becomes narrower with decreasing r_0). Correspondingly, the competition between the inner and outer wells alters in favour of the outer well, resulting in orbital swelling rather than collapse.

What about the range of $1.45 < r_0 < 1.59$, where our calculations of $P_{1s}(r)$ and E_{1s} have failed? The interpretation is that, for $1.45 < r_0 < 1.59$, both the short-range inner and

long-range outer wells have about the same binding strength for the 1s electron. Correspondingly, $P_{1s}(r)$ should possess two maxima of not too dissimilar amplitudes, one in each of the wells. Earlier, such a rare occurrence was found to emerge naturally in nf series of Ba$^+$ [10, 13] and in compressed Cr [11, 12]. It becomes extremely difficult to obtain the solution of the Schrödinger or Hartree–Fock equation in this parameter range, where a standard computer algorithm becomes unstable; see corresponding discussion in [10], or a brief discussion and references in [11].

It appears that not only the ground state but also excited states of confined hydrogen can experience atomic swelling. This is clearly demonstrated by figures 3 and 4, where the P_{2p} and P_{3p} radial functions of hydrogen compressed by the square-well potential with $r_0 = 1.45$ (figure 3) and $r_0 = 1.59$ (figure 4) are depicted. Let us discuss the displayed calculated data for $r_0 = 1.45$ and $r_0 = 1.59$ separately, along with their significance for the photoabsorption spectra of the compressed atom.

Exploring figure 3 ($r_0 = 1.45$), one can see, first, that the excited P_{2p} orbital peaks at $r \approx 12$ versus $r \approx 4$ for free hydrogen. Thus, the size of the H(2p)@U_c atom is three times the size of the excited free atom—a clear evidence of atomic swelling of excited states under confinement. Second, highly spectacular, the excited P_{2p} and ground-state P_{1s} functions of H@U_c appear to be about the same and peak at about the same value of r. The overlap between P_{2p} and P_{1s} becomes huge, compared to that of the free atom. This results in an abnormally large oscillator strength $f_{1s \to 2p}$ of the 1s $\to$ 2p

Figure 4. Radial functions $P_{1s}(r)$, $P_{2p}(r)$ and $P_{3p}(r)$ of free hydrogen and hydrogen confined by the square-well potential U_c with $U_0 = 2.5$, $r_0 = 1.59$ and $\Delta = 5$ au, as marked.

transition in H@U_c. Indeed, the calculation shows that, in H@U_c, $f_{1s \to 2p} \approx 0.812$ versus $f_{1s \to 2p} \approx 0.416$ in free hydrogen. As known, the sum of all oscillator strengths of $n\ell \to n'(\epsilon)\ell \pm 1$ transitions from an atomic $n\ell$ subshell into its discrete and continuum spectra equals the number of electrons in the subshell. Hence, in our case, over 80% of the total oscillator strength of H@U_c belongs to a single transition $1s \to 2p$—a bizarre property of the atom under penetrable confinement. Note, earlier [14, 15], the abnormally large value of $f_{1s \to 2p} \approx 1$ of hydrogen was predicted upon its confinement inside an impenetrable well ($U_0 = \infty$, $D = \infty$) of a small radius r_0. This, however, is not surprising, since the impenetrable confinement *does* actually compress the atom by driving the 2p orbital closer to the 1s one.

By exploring figure 4 ($r_0 = 1.59$), one can see that, due to atomic swelling, the excited P_{2p} and P_{3p} orbitals of H@U_c peak at $r > 10$ whereas the ground-state function P_{1s} peaks compactly near $r \approx 1$, as in the free atom (there is no atomic swelling for the ground-state hydrogen at $r_0 = 1.59$). Furthermore, in H@U_c, $P_{2p} \approx 0$ and $P_{3p} \approx 0$ everywhere where $P_{1s} \neq 0$, in contrast to P_{1s}, P_{2p} and P_{3p} in the free atom. Hence, the overlap between P_{1s} and P_{np} functions in H@U_c is practically zero, thereby making $f_{1s \to np} = 0$, in the compressed atom. Correspondingly, the compressed atom loses its $1s \to n'\ell \pm 1$ discrete photoabsorption spectrum. Hence, the only possibility for H(1s)@U_c to absorb a photon is exclusively through its photoionization.

Thus, the spectra of the free hydrogen, hydrogen under confinement with $r_0 = 1.59$ and hydrogen under confinement with $r_0 = 1.45$ are distinctly different from each other, both qualitatively and quantitatively.

In conclusion, the discussion in the present paper has dealt with the atomic structure and photo-spectra of hydrogen under compression by a repulsive penetrable spherical potential $U_c(r)$ of a certain height U_0, thickness Δ and inner radius r_0. The tendency of sudden atomic swelling, rather than contraction, upon increasing pressure has been discovered. Profoundly distinct impacts of atomic swelling on the photo-spectra of hydrogen under confinement have been demonstrated. Specifically, it has been unravelled that atomic swelling can result either in the loss of a discrete photoabsorption spectrum of the atom, or, on the contrary, in its significant gain, depending on pressure (i.e. the confinement radius r_0). The findings have been exemplified using arbitrarily chosen values of U_0 and Δ. However, some critical values of U_0 and Δ below which the effects will vanish are anticipated. This will happen when U_0 and Δ are such that the confining potential fails to push atomic levels up to the degree needed for the electron to jump from a narrow inner binding well of the effective potential $U_{1s}^{eff}(r)$ into its outer binding well (see figure 2) at any r_0. Other than that, the discovered effects must persist for a broad range of U_0 and Δ values. As a follow-up study, it would be interesting to learn how atomic swelling develops in a multielectron atom, where not just one electron but two or more electrons might jump from the inner well into the outer well of $U^{eff}(r)$ at a certain critical value of r_0, how the effect could affect electron correlation in the atom, as well as how all this could modify the interaction of radiation with such a compressed multielectron atom relative to the free atom. The authors are currently working on these topics. As for the present paper, its sole aim has been to demonstrate the existence and importance of atomic swelling itself, as the first step towards the understanding of what might happen in atoms confined by repulsive spherical potentials of finite thickness.

As an example of the practical significance of the results of this study, the latter, according to [16], may be helpful in understanding the progressive confinement and loss of electrons in some dense metal systems.

References

[1] Michels A, de Boer J and Bijl A 1937 *Physica* **4** 981
[2] Sommerfeld A and Welker H 1938 *Ann. Phys.* **32** 56
[3] Jaskólski W 1996 *Phys. Rep.* **271** 1
[4] Buchachenko A L 2001 *J. Phys. Chem.* B **105** 5839
[5] Dolmatov V K, Connerade J-P, Baltenkov A S and Manson S T 2004 *Radiat. Phys. Chem.* **70** 417
[6] Sabin J R, Brändas E and Cruz C A (ed) 2009 *Advances in Quantum Chemistry: Theory of Confined Quantum Systems. Part 1* vol 57 (New York: Academic) pp 1–334

J. Phys. B: At. Mol. Opt. Phys. **45** (2012) 225003

V K Dolmatov and J L King

[7] Sabin J R, Brändas E and Cruz C A (ed) 2009 *Advances in Quantum Chemistry: Theory of Confined Quantum Systems. Part 2* vol 58 (New York: Academic) pp 1–297

[8] Connerade J-P, Dolmatov V K and Manson S T 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** L275

[9] Connerade J-P, Dolmatov V K and Manson S T 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** L395

[10] Connerade J-P 1998 *Highly Excited Atoms* (Cambridge: Cambridge University Press)

[11] Connerade J-P and Dolmatov V K 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 3557

[12] Connerade J-P, Dolmatov V K and Lakshmi P A 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** 251

[13] Connerade J-P and Mansfield M W D 1975 *Proc. R. Soc.* A **346** 565

[14] Laughlin C 2004 *J. Phys. B: At. Mol. Opt. Phys.* **37** 4085

[15] Stevanović L 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 165002

[16] Wallace J 2012 private communication