Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Nuclear Physics A 790 (2007) 784c–787c
NUCLEAR PHYSICS A

Helium atom in a box: a fully quantal solution

D. M. Mitnik [a] *

[a]Departmento de Física, FCEyN, Universidad de Buenos Aires, and Instituto de Astronomía y Física del Espacio (IAFE), Casilla de Correo 67, Sucursal 28, (C1428EGA) Buenos Aires, Argentina.

A complete non–perturbative solution of the Helium atom in a box problem is presented by developing two numerical techniques. The first technique is the direct solution by diagonalization of the Hamiltonian, and the second is based on a constrained relaxation of the wave functions. Time–dependent propagation of doubly–excited wave–functions is analyzed, allowing the calculation and the visualization of the autoionization process.

1. INTRODUCTION

The use of discrete numerical methods to solve a real atomic–physical problem transforms it, in fact, in the solution of a spatially confined system problem. In this way, the *Helium atom in a box* problem represents the search for the Helium ion wavefunctions by using finite and discrete numerical lattice methods. This method turns out to be a very good approximation to the physical bound states for all orbitals that fit well into the lattice (i.e., for such bound states in which the wave function at the boundaries approaches zero in a practical sense for numerical calculations). It also gives particularly true continuum solutions of the ion, not necessarily confined inside a box.

2. THEORY: CLOSE–COUPLING REPRESENTATION FOR THE REAL HELIUM HAMILTONIAN

In our previous work [1], we presented the solution of the spherical model (or Temkin–Poet model) of the Helium atom. In this work, we have extended our methods with the inclusion of other partial waves through the coupled–channel equations. The full Hamiltonian for the real Helium is

$$H(\vec{r_1},\vec{r_2}) = -\frac{\nabla^2}{2} - \frac{\nabla^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\vec{r_1}-\vec{r_2}|}. \quad (1)$$

Any solution q of the two–electron real Helium Hamiltonian may be expanded as:

$$\Psi_q^{LS}(\vec{r_1},\vec{r_2}) = \frac{1}{r_1 r_2} \sum_{\ell_1,\ell_2} P_q{}^{LS}_{\ell_1\ell_2}(r_1,r_2) \times \sum_{m_1,m_2} C^{l_1 l_2 L}_{m_1 m_2 0} Y_{\ell_1 m_1}(\hat{r_1}) Y_{\ell_2 m_2}(\hat{r_2}), \quad (2)$$

*Research supported partially by grants UBACyT X075 (Universidad de Buenos Aires), PICTR2002 00122 (ANPCyT), and PIP6268 (CONICET). Computational resources are supported by a grant from Scientific Discovery through Advanced Computing (SciDAC) (US Department of Energy), administered by Auburn University, USA.

doi:10.1016/j.nuclphysa.2007.03.026

where $P_q\ {}^{LS}_{\ell_1\ell_2}(r_1, r_2)$ is the two–dimensional reduced radial wave function, $Y_{\ell m}$ are spherical harmonics in the remaining angular coordinates, and $C^{l_1 l_2 L}_{m_1 m_2 0}$ are Clebsch–Gordan coefficients.

The question concerning us is how to represent the Hamiltonian (1) (having two spacial dimensions) as a square matrix operating on a column vector. We chose to unfold the square lattice of points spanning the two spatial dimensions into one column of points. This discretization of the radial space is similar to that used for solving the Temkin–Poet model atom. However, we now have to increase the dimensions in order to include the different (ℓ_1, ℓ_2) channels that couple to the total L. The matrix representation of the Hamiltonian for this basis is written as:

$$\hat{H} = \begin{pmatrix} \left[\begin{array}{c} \hat{H}_{\ell_1\ell_2} \\ + \\ \hat{V}_{\ell_1\ell_2,\ell_1\ell_2} \end{array}\right] & \left[\begin{array}{c} \\ \hat{V}_{\ell_1\ell_2,\ell'_1\ell'_2} \\ \\ \end{array}\right] & \cdots & \left[\begin{array}{c} \\ \hat{V}_{\ell_1\ell_2,\ell''_1\ell''_2} \\ \\ \end{array}\right] \\ \left[\begin{array}{c} \\ \hat{V}_{\ell'_1\ell'_2,\ell_1\ell_2} \\ \\ \end{array}\right] & \left[\begin{array}{c} \hat{H}_{\ell'_1\ell'_2} \\ + \\ \hat{V}_{\ell'_1\ell'_2,\ell'_1\ell'_2} \end{array}\right] & \cdots & \left[\begin{array}{c} \\ \hat{V}_{\ell'_1\ell'_2,\ell''_1\ell''_2} \\ \\ \end{array}\right] \\ & \ddots & & \\ \left[\begin{array}{c} \\ \hat{V}_{\ell''_1\ell''_2,\ell_1\ell_2} \\ \\ \end{array}\right] & \left[\begin{array}{c} \\ \hat{V}_{\ell''_1\ell''_2,\ell'_1\ell'_2} \\ \\ \end{array}\right] & \cdots & \left[\begin{array}{c} \hat{H}_{\ell''_1\ell''_2} \\ + \\ \hat{V}_{\ell''_1\ell''_2,\ell''_1\ell''_2} \end{array}\right] \end{pmatrix} \tag{3}$$

where the blocks $\hat{H}_{\ell_1\ell_2}$ are

$$\hat{H}_{\ell_1\ell_2} = \begin{pmatrix} \left[\begin{array}{ccccccc} h & \alpha & & & & & \\ \alpha & h & \alpha & & & & \\ & \alpha & h & \alpha & & & \\ & & \ddots & & & & \\ & & & \alpha & h & \alpha & \\ & & & & \alpha & h & \end{array}\right] & \left[\begin{array}{ccccccc} \beta & & & & & & \\ & \beta & & & & & \\ & & \beta & & & & \\ & & & \ddots & & & \\ & & & & \beta & & \\ & & & & & \beta & \end{array}\right] & \left[\begin{array}{ccc} & & \\ & & \\ & 0 & \\ & & \\ & & \\ & & \end{array}\right] & \cdots & \left[\begin{array}{ccc} & & \\ & & \\ & 0 & \\ & & \\ & & \\ & & \end{array}\right] \\ \left[\begin{array}{ccccccc} \beta & & & & & & \\ & \beta & & & & & \\ & & \beta & & & & \\ & & & \ddots & & & \\ & & & & \beta & & \\ & & & & & \beta & \end{array}\right] & \left[\begin{array}{ccccccc} h & \alpha & & & & & \\ \alpha & h & \alpha & & & & \\ & \alpha & h & \alpha & & & \\ & & \ddots & & & & \\ & & & \alpha & h & \alpha & \\ & & & & \alpha & h & \end{array}\right] & \left[\begin{array}{ccc} \beta & & \\ & \beta & \\ & & \beta \\ & \ddots & \\ & & \beta \\ & & \end{array}\right] & \cdots & \left[\begin{array}{ccc} & & \\ & & \\ & 0 & \\ & & \\ & & \\ & & \end{array}\right] \\ & \ddots & & & \\ \left[\begin{array}{ccc} & & \\ & & \\ & 0 & \\ & & \\ & & \\ & & \end{array}\right] & \left[\begin{array}{ccc} & & \\ & & \\ & 0 & \\ & & \\ & & \\ & & \end{array}\right] & \cdots & \left[\begin{array}{ccccccc} \beta & & & & & & \\ & \beta & & & & & \\ & & \beta & & & & \\ & & & \ddots & & & \\ & & & & \beta & & \\ & & & & & \beta & \end{array}\right] & \left[\begin{array}{ccccccc} h & \alpha & & & & & \\ \alpha & h & \alpha & & & & \\ & \alpha & h & \alpha & & & \\ & & \ddots & & & & \\ & & & \alpha & h & \alpha & \\ & & & & \alpha & h & \end{array}\right] \end{pmatrix} \tag{4}$$

with

$$\begin{aligned} h &= \frac{1}{\Delta r_1^2} + \frac{1}{\Delta r_2^2} - \frac{Z}{i \times \Delta r_1} - \frac{Z}{j \times \Delta r_2} + \frac{\ell_1(\ell_1+1)}{2(i \times \Delta r_1)^2} + \frac{\ell_2(\ell_2+1)}{2(j \times \Delta r_2)^2} \ , \\ \alpha &= -\frac{1}{2}\frac{1}{\Delta r_1^2} \quad \text{and} \quad \beta = -\frac{1}{2}\frac{1}{\Delta r_2^2} \ . \end{aligned} \tag{5}$$

The matrices $\hat{V}_{\ell_1\ell_2,\ell_1'\ell_2'}$ are diagonal, and they are written as:

$$\hat{V}_{\ell_1\ell_2,\ell_1'\ell_2'(ss)} = (-1)^{L+\ell_2+\ell_2'}\sqrt{(2\ell_1+1)(2\ell_1'+1)(2\ell_2+1)(2\ell_2'+1)} \times \sum_\lambda \frac{r_<^\lambda}{r_>^{\lambda+1}} \begin{pmatrix} \ell_1 & \lambda & \ell_1' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_2 & \lambda & \ell_2' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & \ell_2' & \ell_1' \\ \lambda & \ell_1 & \ell_2 \end{Bmatrix}, \quad (6)$$

where $r_>$ ($r_<$) is the biggest (smallest) between $r_1 = i \times \Delta r_1$ and $r_2 = j \times \Delta r_2$.

3. RESULTS

3.1. Wave–functions and energies

We developed two methods for solving the problem. In the first one, the complete set of wave functions corresponding to the Helium atom were obtained from the direct diagonalization of the matrix. In order to allow the diagonalization of such large matrices, we wrote the computer programs to use on distributed–memory parallel computers. The Hamiltonian matrix was directly partitioned over the many processors, so memory requirements per processor was minimized and scalability in time thus achieved. The procedure used in the parallelization of the codes is similar to that employed for the parallelization of the R–matrix package [2].

In the second method (the relaxation method) the energies and wave functions are calculated by relaxation of an initial wave function Φ in a fictitious imaginary time $\tau = it$. That means a transformation of the time–dependent Schrödinger equation into a diffusion equation. The net result from this imaginary time propagation is the enhancement of those components of the solution with smaller eigenvalues of H relative to those with larger eigenvalues. Doubly–excited autoionizing states are calculated by imposing additional constraints at the iteration of the relaxation, projecting out also the one–electron $1s$ component of the wave functions [1,3].

Details of the result dependence on the numerical grid, and the different number of coupled channels are found in [4]. In principle, the methods outlined here are exact, and we can obtain solutions with arbitrary precision. However, our intention in the present work has not been to obtain the best energies and wave functions for the helium atom. Instead, we are interested in presenting a complete solution to the problem which could be used to understand the nature and physical significance of many–body interactions in confined atomic systems. We are interested also in the calculation of such atomic processes which are strongly dependent of these interactions.

3.2. Time–dependent Propagation

Figure 1 shows the evolution of the probability density of the wave function $\Phi_{2s^2}(t)$, under the time–propagation with the Schrödinger equation

$$\Phi_{2s^2}(t) = e^{-i\hat{H}t}\Phi_{2s^2}(t_0), \quad (7)$$

where $\Phi_{2s^2}(t_0)$ is the wave function Φ_{2s^2} obtained by the constrained relaxation method. The pictures show how the initial pure $2s^2$ wave function acquires a continuum feature, as it evolves in time. At the beginning, a slow deformation of the wave developes, with the probability dropping towards the wings of the wave. Then, the characteristic pattern of a $1sks$ continuum wave is formed at the axes, advancing rapidly to the box borders.

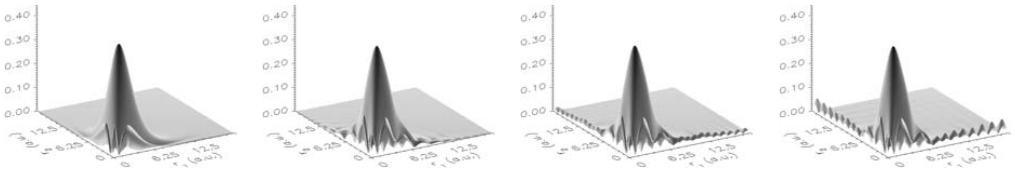

Figure 1. Snapshots of the total wave function amplitude $|\Phi(t)| = |e^{-i\frac{H}{\hbar}t}\Phi(0)|$ at times 0, 5, 10 and 15 a.u., during the autoionization process.

Information about the temporal evolution of each channel is given in Figure 2, where the $(l_1, l_2) = ss$, pp and dd channels are displayed separately, at $t = 5$ a.u.. The full movies for the propagation can be downloaded at the author's personal webpage¶.

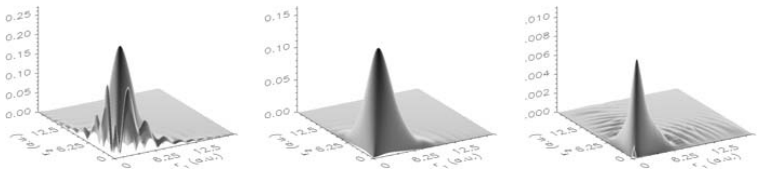

Figure 2. Snapshots of the function amplitude $|\Phi_{l_1,l_2}(t)| = |e^{-i\frac{H}{\hbar}t}\Phi_{l_1,l_2}(0)|$ at time $t = 4.5$ a.u., during the autoionization process, for the $(l_1, l_2) = ss$, pp and dd channels.

REFERENCES

1. D.M. Mitnik, Phys Rev. A 70 (2004) 022703.
2. D.M. Mitnik, M.S. Pindzola, D.C. Griffin, and N.R. Badnell, J. Phys. B 32 (1999) L479.
3. D.M. Mitnik, D.C. Griffin, and M.S. Pindzola, Phys. Rev. Lett. 88 (2002) 173004.
4. D.M. Mitnik and J.E. Miraglia, J. Phys. B 38 (2005) 3325.

¶http://www.df.uba.ar/users/dmitnik