

## Convergent Energy States and Wave Functions of Helium Atom in an $L^2$ Basis

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### Abstract

The convergence of energy states and wave functions of helium atom is presented. The energy states are obtained by diagonalizing the helium Hamiltonian in a non-orthogonal Laguerre basis. Some of the energy states will be exact discrete eigenstates, others will be a discrete representation of the continuum states. As the basis size  $N$  increases the lowest bound states in energy states converge to the exact eigenstates, whereas the positive energy states provide an increasingly dense discretization of the continuum. The convergence of wave functions is obtained by the Gauss-Pollaczek quadrature method.

**Keywords :** Diagonalization, Hamiltonian, non-orthogonal Laguerre, Gauss-Pollaczek quadrature

### Abstrak

Telah dikaji konvergensi tingkat energi dan fungsi keadaan atom helium. Tingkat energi diperoleh dengan mendiagonalisasikan Hamiltonian helium terhadap basis Laguerre non-orthogonal. Beberapa dari tingkat energi akan diperoleh dalam bentuk energi diskrit eksak, yang lainnya berupa tingkat energi kontinu yang dinyatakan dalam bentuk diskrit. Jika jumlah basis  $N$  ditambah, tingkat energi terikat konvergen terhadap tingkat energi eksak, sedangkan tingkat energi kontinu positif memperoleh penambahan jumlah yang banyak dalam bentuk diskrit. Konvergensi untuk fungsi keadaan diperoleh dengan metode Gauss-Pollaczek quadrature.

**Kata kunci :** Diagonalisasi, Hamiltonian, Laguerre non-orthogonal, Gauss-Pollaczek quadrature

### 1. Introduction

Atomic collision phenomena are of fundamental importance in atomic and molecular physics. The understanding of atomic collision phenomena requires the complete information of the energy states and wave functions of the target atom. Our study of many-electron atoms is started by considering the simplest one, namely atoms (or ions) consisting of a nucleus of charge  $Ze$  and two electrons, specially the helium atom. Our discussion is limited to the non-relativistic theory of two-electron atoms. Schrödinger's equations cannot be solved exactly for two-electron atoms or ions, so that approximation methods with a finite basis of  $L^2$  type must be used. The  $L^2$  method which uses square integrable functions has been the subject of considerable study for solutions of quantum scattering problems. In this model one uses a finite basis of  $L^2$  functions to diagonalize the target Hamiltonian which has a discrete spectrum of  $L^2$  wave functions corresponding to the bound states and in addition

a continuous spectrum of positive energy states. The diagonalization in the finite  $L^2$  bases gives both negative and positive energy states. The basis is usually chosen so that the lowest-lying channels are described adequately while the other bound states are collectively approximated by remaining negative energy eigenvectors. The positive energy eigenstates and associated  $L^2$  eigenfunctions in some way approximate the target continuum. A new method for performing scattering calculations entirely with the  $L^2$  functions of Laguerre types began when Heller and Yamani<sup>1)</sup> attempted to take full advantage of the analytic properties of a given Hamiltonian and also of the  $L^2$  basis which is used to describe the wave function. Specifically, they develop the basic theory using Laguerre-type basis functions appropriate for s-wave scattering. Since Yamani and Reinhardt<sup>2)</sup> who developed a systematic approach to illustrate the mathematical sense in which the  $L^2$  functions would approximate continuum scattering solutions, the  $L^2$  functions of Laguerre type have been widely applied to

describe the scattering processes. Stelbovics and Winata<sup>3)</sup> have also studied and examined the convergence rates of  $L^2$  expansion of Laguerre types. They showed that the  $L^2$  wave function converges to the exact Coulomb wave function in the space coordinate representation. It is the purpose of our attention to present a study of the  $L^2$  expansion methods for the helium atom system.

## 2. Theory

Hamiltonian  $H_T$  of the non-relativistic helium target can be written as<sup>4)</sup>

$$H_T = H_1 + H_2 + V_{12}, \quad (2.1)$$

where

$$H_i = K_i + V_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}, \quad (2.2)$$

for  $i = 1, 2$ , are the one-electron Hamiltonians of the  $\text{He}^+$  ion, and

$$V_{12} = \frac{1}{|r_1 - r_2|}, \quad (2.3)$$

is the electron-electron potential. Atomic units are assumed throughout.

We use the L-S coupling scheme, and so the helium wave functions  $\Phi^{ls\pi}$  are characterized by the orbital angular momentum  $l$ , spin  $s$ , and parity  $\pi$ . One-electron orbitals  $\varphi_\alpha(x)$ , which are used to build the two-electron basis, are the product of radial functions, spherical harmonics, and spin functions ( $\sigma = \pm 1/2$ )

$$\varphi_\alpha(x) = \frac{1}{r} \phi_{k_\alpha l_\alpha}(r) Y_{l_\alpha m_\alpha}(\hat{r}) \chi(\sigma). \quad (2.4)$$

Notation of  $\alpha$  and  $\beta$  are used to denote first and second electron. Here  $x$  is used to denote both the spatial and spin coordinates. The radial part of the single-particle functions we take to be the non-orthogonal basis

$$\phi_{kl}(r) = (\lambda_l r)^{l+1} \exp(-\lambda_l r / 2) L_k^{2l+1}(\lambda_l r) \quad (2.5)$$

where the  $L_k^{2l+1}(\lambda_l r)$  are the associated Laguerre polynomials, and  $k$  ranges from 1 to the basis size  $N$ .

For brevity of notation we denote helium states by  $\Phi_n^{ls\pi}(x_1, x_2)$ , where  $n = 1, \dots, N$ , with corresponding orbital angular momentum  $l = l_n$ , spin  $s = s_n$ , and parity  $\pi = \pi_n$ , which may be written as

$$\begin{aligned} \Phi_n^{ls\pi}(x_1, x_2) \\ = \sum_{n_\alpha, m_\beta} C_{\alpha\beta}^{(n)} |\varphi_\alpha(x_1) \varphi_\beta(x_2); \pi_n l_n m_s m_s \rangle. \end{aligned} \quad (2.6)$$

Here the configuration interaction (CI) coefficients  $C_{\alpha\beta}^{(n)}$  satisfy the symmetry property

$$C_{\alpha\beta}^{(n)} = (-1)^{l_\alpha + l_\beta - l_n - s_n} C_{\beta\alpha}^{(n)} \quad (2.7)$$

to ensure antisymmetry of two-electron target states. The two-electron functions in (2.6) are given by

$$\begin{aligned} |\varphi_\alpha(x_1) \varphi_\beta(x_2); \pi l m_s m_s \rangle \\ = \frac{1}{r_1 r_2} \phi_{k_\alpha l_\alpha}(r_1) \phi_{k_\beta l_\beta}(r_2) |l_\alpha l_\beta : l m \rangle X(sm_s) \end{aligned} \quad (2.8)$$

where  $\pi = (-1)^{l_\alpha + l_\beta}$ ,

$$|l_\alpha l_\beta : l m \rangle = \sum_{m_\alpha, m_\beta} C_{l_\alpha l_\beta l}^{m_\alpha m_\beta m} Y_{l_\alpha m_\alpha}(\hat{r}_1) Y_{l_\beta m_\beta}(\hat{r}_2), \quad (2.9)$$

and the two-electron spin function is defined by

$$X(sm_s) = \sum_{\sigma_1, \sigma_2} C_{\frac{1}{2} \frac{1}{2} s}^{\sigma_1 \sigma_2 m_s} \chi(\sigma_1) \chi(\sigma_2). \quad (2.10)$$

The target states  $\Phi_n^{ls\pi}(x_1, x_2)$  satisfy

$$\langle \Phi_m | H_T - E_n | \Phi_n \rangle = 0, \quad (2.11)$$

where  $E_n$  is the energy associated with  $\Phi_n^{ls\pi}(x_1, x_2)$ .

Calculation of equation (2.11) without the electron-electron potential leads to the recurrence formula

$$\begin{aligned} 2 \left[ \left( k_\alpha + l_\alpha + 1 - \frac{Z}{\lambda_\alpha} \right) X + \frac{2Z}{\lambda_\alpha} \right] C_{k_\alpha, k_\beta}^* \\ - (k_\alpha + 2l_\alpha + 1) C_{k_\alpha - 1, k_\beta}^* \\ - (k_\alpha + 1) C_{k_\alpha + 1, k_\beta}^* = 0, \end{aligned} \quad (2.12)$$

where

$$X = \frac{(k_\beta + l_\beta + 1)(8E - \lambda_\alpha^2 - \lambda_\beta^2) + 4Z\lambda_\beta}{(k_\beta + l_\beta + 1)(8E + \lambda_\alpha^2 - \lambda_\beta^2) + 4Z\lambda_\beta}, \quad (2.13)$$

and

$$C_{k_\alpha, k_\beta}^* = \frac{\Gamma(k_\alpha + 2l_\alpha + 2) \Gamma(k_\beta + 2l_\beta + 2)}{\Gamma(k_\alpha + 1) \Gamma(k_\beta + 1)}. \quad (2.14)$$

Calculation of the correction factor for the recurrence formula is made by the electron-electron potential given as follows

$$\langle \Phi_m | \frac{1}{|r_1 - r_2|} | \Phi_n \rangle = \sum_l f_k(r_1, r_2) [(2l_\alpha + 1)(2l_\beta + 1)]^{\frac{1}{2}} \left( \frac{4\pi}{2l + 1} \right) \langle l_\alpha | Y_{lm} | l_\alpha \rangle \langle l_\beta | Y_{lm} | l_\beta \rangle \langle (l_\alpha l) l_\alpha, l_\beta : l | l_\alpha, (l_\beta) l_\beta : l \rangle \quad (2.15)$$

where

$$f_k(r_1, r_2) = \frac{\lambda_\alpha^{k+1}}{\lambda_\beta^k} \sum_{n=0}^{k_\alpha} \left[ \frac{(k+1)_n}{(n!)} \right]^2 \frac{\Gamma(k_\alpha - n + 2l_\alpha - k + 1)}{\Gamma(k_\alpha - n + 1)} \sum_{m=0}^{k_\beta} \left[ \frac{(-k)_m}{(m!)} \right]^2 \frac{\Gamma(k_\beta - m + 2l_\beta + k + 2)}{\Gamma(k_\alpha - m + 1)}. \quad (2.16)$$

The Gauss-Pollaczek quadrature formula to ensure the completeness of eigenfunctions is given by<sup>5)</sup>

$$\int_a^b F(x) d\mu(x) = \sum_i^N W_{Ni} F(X_{Ni}) \quad (2.17)$$

the limit  $a$  and  $b$  comprise any interval which covers the point and continuum spectrum mapped into  $X$  variables.  $W_{Ni}$  are associated quadrature weight which are given by

$$W_{Ni} = \frac{\lambda_1 \lambda_2 \dots \lambda_N}{p_{N-1}(x_{Ni}) \frac{d}{dx} p_N(x_{Ni})}. \quad (2.18)$$

### 3. Result and Discussions

In Table 3.1. energy states which are produced from  $L^2$  expansions are shown for  $l = 0$  and  $\lambda_\alpha = 4.0 a^{-1}$ ,  $\lambda_\beta = 1.02 a^{-1}$ , and different bases sizes  $N = 10$  and  $11$ . The choice of  $\lambda_\alpha = 4.0 a^{-1}$ ,  $\lambda_\beta = 1.02 a^{-1}$  ensures that the first three states converge to the true  $1^1S$ ,  $2^3S$ ,  $2^1S$  helium atom bound states.

Table 3.1. Energy states which are produced from  $L^2$  expansions for basis sizes  $N = 10$  and  $11$ .

$N$	$i$	Energy states	$E_{Ni}$ (a.u.) (Calculation results)	$E$ (a.u.) (Experimen results) (Moore, 1971) <sup>6)</sup>
10	1	$1^1S$	-2.903710	-2.903720
	2	$2^3S$	-2.175411	-2.175230
	3	$2^1S$	-2.145751	-2.145970
	4		-1.896700	
	5		-0.396721	
	6		0.012680	
	7		0.219081	
	8		0.606900	
	9		3.108415	
	10		8.364555	
11	1	$1^1S$	-2.903710	-2.903720
	2	$2^3S$	-2.175411	-2.175230
	3	$2^1S$	-2.145751	-2.145970
	4		-1.896700	
	5		-0.396721	
	6		0.012680	
	7		0.219081	
	8		0.606900	
	9		3.108415	
	10		8.364555	
	11		9.367666	

In Table 3.2. the values of  $W_{Ni}$  are shown for  $\lambda_\alpha = 1.02 a^{-1}$ ,  $\lambda_\beta = 0.0 a^{-1}$  and different basis sizes  $N = 1, 5,$  and  $10$ . The table shows the weight calculated by equation (2.18). Looking at Table 3.2, it is clear that for chosen basis only the ground state will contribute a negative weight.

Table 3.2. The Gauss-Pollaczek quadrature weight of  $L^2$  expansion in the finite basis for different basis sizes  $N=1,5,10$ . Powers of ten are denoted by the numbers in brackets.

$N$	$i$	$W_{Ni}$	$\sum_i^N W_{Ni}$	$X_{Ni}$
1	1	-.1634910463(+1)	-.1634910463(+1)	.2040816327(+1)
5	1	-.1729606085(+1)	-.1634910463(+1)	+1.703620224(+1)
	2	+7773932765(-2)		-.5050495050(+2)
	3	+7457191089(-2)		-.2438986170(+1)
	4	+1858863495(-1)		-.7987655172(+0)
	5	+6087568342(-1)		+5864060803(+0)
10	1	-.1733402595(+1)	-.1634910463(+1)	+1.703068009(+1)
	2	+7773932765(-2)		-.5050495050(+2)
	3	+6310892815(-2)		-.2491534568(+1)
	4	+2733938325(-2)		-.1626246288(+1)
	5	+3490662992(-2)		-.1224730895(+1)
	6	+6301203019(-2)		-.7411483106(+0)
	7	+1084137596(-1)		-.2068158782(+0)
	8	+1783041170(-1)		+2946584980(+0)
	9	+2492564429(-1)		+6917840074(+0)
	10	+1828407030(-1)		+9315687946(+0)

#### 4. Conclusions

Numerical calculations of recurrence formula in equation (2.12) and (2.15) resulted in the energy states. Some of them are exact discrete eigenstates, whilst others are discrete representations of the continuum states. As the basis sizes  $N$  increases, the lowest bound states in energy states converge to the exact eigenstates, whereas the positive energy states provide an increasingly dense discretization of the continuum. The completeness of eigenfunctions was derived in terms of the Gauss-Pollaczek quadrature rule. It is shown that the total weight converges to the same number for different basis size. The convergence of related work functions is clearly indicated by the first weight in the Tabel 3.2 which relates to the ground state.

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