

A numerical basis for the accurate representation of the continuum spectrum of atomic Hamiltonians

L.A.A. Nikolopoulos

Department of Telecommunication Science & Technology, University of Peloponnese,
GR-221 00, Tripolis, Greece

E-mail: nlambros@uop.gr

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We present a method for the accurate calculation of the complete spectrum of the Schrödinger equation in terms of *B*-splines polynomial basis. The method is capable to represent numerically the bound and continuum spectrum of complex atomic systems. The theoretical method is discussed, and an application to hydrogenic Hamiltonian is given.

KEY WORDS: Schrödinger equation, B splines, photoionization

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1. Bound and continuum states of atomic systems: an overview

In the case of an atom with one electron outside a closed shell, the solution of the stationary Schrödinger equation (SE) can proceed as follows: Exploiting the spherical symmetry of the potential, the wavefunction of the electron is written as $\phi_{\ell m m_s}(\mathbf{r}) = (1/r)P_{\ell l}(r)Y_{lm}(\theta, \phi)\sigma_{m_s}$, with $Y_{lm}(\theta, \phi)$ the usual spherical harmonics and σ_{m_s} , the spin-function. Then the radial SE may be written as:

$$[h_l(r) - \epsilon]P_{\ell l}(r) = \left[-\frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} + V_l(r) - \epsilon \right] P_{\ell l}(r) = 0 \quad (1)$$

The above equation is supplemented with the appropriate boundary conditions (BC) for the bound and the continuum states which, for convential potentials $rV_l(r) \rightarrow Z_{\text{eff}}$, $r \rightarrow \infty$, are given by the following relations:

$$P_{\ell l}(r \rightarrow 0) \rightarrow C_{\ell l} r^{l+1} \rightarrow 0 \quad (2)$$

while for that the infinity the asymptotic conditions read:

$$\begin{aligned} P_{\ell l}(r \rightarrow \infty) &\rightarrow A_{\ell l} e^{-\sqrt{-2\epsilon}r}, \quad \epsilon \leq 0 \\ P_{kl}(r \rightarrow \infty) &\rightarrow aF_{kl}(r) + bG_{kl}(r) = A_{\ell l} \sin \left[kr - l\frac{\pi}{2} + \phi_C + \delta_{kl} \right], \quad \epsilon \geq 0 \end{aligned} \quad (3)$$

with $F_{kl}(r)$, $G_{kl}(r)$ being the regular and irregular Coulomb function, k being the momentum vector of the continuum state related with the energy $\epsilon = k^2/2$, $\phi_C(r)$ the Coulomb phase shift (long-range phase shift) and $\delta_{kl}(r)$ being the scattering phase shift (short-range), which basically reflects the deviation of the true potential ‘seen’ by the outgoing electron $V_l(r)$ from the Coulomb potential $V_C = -Z_{\text{eff}}/r$. Given that, $V_l(r) \rightarrow V_C r \rightarrow \infty$ it is justified the distinction between ‘long-range’ or ‘Coulomb’ and ‘short-range’ or ‘scattering’ phase shift. The Coulomb phase shift is known analytically and given by:

$$\phi_C(r) = \frac{Z_{\text{eff}}}{k} \ln(2kr) + \arg\Gamma\left(l + 1 - i \frac{Z_{\text{eff}}}{k}\right). \quad (4)$$

The amplitudes $A_{\epsilon/kl}$, $C_{\epsilon/k}$ are determined through the appropriate normalization of the bound and continuum solutions. Note that we use the notation $P_{\epsilon l}(r)$, $P_{kl}(r)$ for the bound and continuum states, respectively. The above asymptotic limits holds unchanged for the case of negative ions. Then the asymptotic charge is zero ($\phi_C = 0$) and the asymptotic limit of $P_{kl}(r)$ coincides with a linear combination of Bessel functions.

At this point is obvious that the whole effort for the solution of the SE is reduced to the determination of the radial wavefunction $P_{\epsilon/kl}(r)$. Moreover, the implementation of the above boundary conditions (BC) ensures the following orthonormalization properties of the solutions:

$$\begin{aligned} \langle P_{nl} | P_{ml} \rangle &= \delta_{nm}, \\ \langle P_{\epsilon l} | P_{\epsilon' l} \rangle &= \delta(\epsilon - \epsilon'). \end{aligned}$$

1.1. Rayleigh-Ritz-Galerkin approach

Expanding the radial wavefunctions in a finite basis set (Gaussian, Slater, B-splines, . . .), defined in an interval $[0, R]$, $0 < R < \infty$, (for Gaussian and Slater basis, R extends to infinity) as:

$$P_{\epsilon l}(r) = \sum_{i=1}^{n_s} C_i^{(\epsilon l)} u_i(r), \quad (5)$$

where, n_s is the number of basis $u_i(r)$. Substituting this expansion to the radial SE (1), and taking the variational condition in respect of the coefficients C_i , $\delta \langle u_j(r) | (h_l(r) - \epsilon) | \sum_i^{n_s} C_i^{(\epsilon l)} u_i(r) \rangle = 0$ leads to the following matrix equations for the coefficients $\mathbf{C}_{\epsilon l} = (c_0^{(\epsilon l)}, c_1^{(\epsilon l)}, \dots, c_{n_s}^{(\epsilon l)})$:

$$\mathbf{A}_l(\epsilon) \cdot \mathbf{C} = [\mathbf{h}_l - \epsilon \mathbf{U}] \cdot \mathbf{C}_{\epsilon l} = 0. \quad (6)$$

The matrix \mathbf{h}_l is the representation of the radial Hamiltonian on the finite basis, and U the overlap matrix, defined by,

$$h_{ij} \equiv \langle u_i | h_l(r) | u_j \rangle = \int_0^R dr u_i(r) h_l(r) u_j(r), \quad (7)$$

$$u_{ij} \equiv \langle u_i | u_j \rangle = \int_0^R dr u_i(r) u_j(r). \quad (8)$$

The boundary conditions for the bound states define a *two-point boundary value* problem, whose solution give discrete eigenfunctions and eigenvalue energies, whereas the boundary conditions for the continuum states define an *initial value* problem for each arbitrary pre-selected energy $\epsilon = k^2/2$. More over, the ‘box’ hamiltonian \mathbf{h}_l , for the case that R has finite value, is well known that is non-hermitian due to kinetic term $-d^2/dr^2$.

$$h_{ij} = \frac{1}{2} \langle u'_i | u'_j \rangle - \langle u_i | \frac{l(l+1)}{2r^2} + V_l(r) | u_j \rangle + \left[\frac{1}{2} u_i(r) u'_j(r) \right]_0^R = \hat{h}_{ij} + h_{ij}^S, \quad (9)$$

where $\hat{\mathbf{h}}$ is the symmetric part of the Hamiltonian and h_S is the surface term, vanishing in the limit $R \rightarrow \infty$, with algebraic form given by the Bloch operator:

$$h_S = \frac{1}{2} \delta(r) \frac{\partial}{\partial r} (r \cdot). \quad (10)$$

2. Artificial boundary conditions: $\alpha P_{\epsilon/kl}(R) + \beta P'_{\epsilon/kl}(R) = 0$

Especially for numerical computations one has to introduce the finite value R , thus effectively replacing the infinity for a practical investigation of the problem. The most reasonable choice for the value of this finite boundary R is to be so large that its finite value to introduce negligible error for all practical purposes of the specific problem under question. An alternative approach is to impose the boundary conditions to this artificial boundary, resulting to an approximate finite representation of the true hamiltonian inside this boundary spherical box. Those artificial boundary conditions provide the necessary link between the ‘interior’ and the ‘exterior’ region. A set of homogeneous BC may be the following:

$$\alpha P_{\epsilon/kl}(R) + \beta P'_{\epsilon/kl}(R) = 0. \quad (11)$$

For specific values of α and β the constraint (11) selects from the total spectrum of the allowed wavefunctions (bound and continuum) those that this constraint is satisfied. For states with negative energy $\epsilon \leq 0$ (bound states), which the allowed spectrum is already discrete, it forces a change in the function shape (prominent, near the boundaries) together with an energy shift. For

states, with positive energy $\epsilon \geq 0$ (scattering states), this constraint makes the continuous spectrum, a denumerably infinite subset of the physical one, since certain continuum discrete states are obtained. Different sets of discrete wavefunctions may be obtained depending on the value of α, β, R parameters. For example, enlargement of the boundary distance R makes the continuum spectrum to crowd more densely toward the limiting value $\epsilon \rightarrow 0$. Moving the artificial boundaries in higher distances, the bound states, eventually, are influenced less and less.

2.1. Bound spectrum: fixed Boundary Conditions: $\beta = 0 \Leftrightarrow P_{\epsilon/kl}(R) = 0$

Assuming as BC $\beta = 0$ we select the wavefunctions having a node on the boundary $P_{\epsilon/kl}(R) = 0$. Physically this is equivalent to assuming a potential of infinite height at the boundaries. This eliminates the surface term, thus transforming the matrix equations (6) to a generalized symmetric eigenvalue problem, where the eigenvalues obtained simultaneously with the corresponding eigenvectors $(\epsilon_i^{(l)}, C_{\epsilon,l})$.

Obtaining the continuum discretized eigenstates this way, degeneracy between continua with different angular quantum number is lost. More over the density of the spectrum is completely uncontrolable and it mainly depends on the box size (R).

If, however, a sufficiently dense discrete spectrum of positive solutions has been obtained, there are many physical problems, for which this lack of degeneracy either does not pose any serious obstacle in the calculations or can be circumvented through certain methods (i.e. interpolation within the energy spectrum. This approach has been followed in a series of works last decade in large variety of problems [1–4].

In figure 1 we show the hydrogen ($Z_{\text{eff}} = 1$) 1s,2s,2p,3p states obtained assuming the fixed boundaries approach.

3. Continuum spectrum: free boundary conditions method

While for the continuum spectrum we also can assume the fixed boundaries method we have followed an alternate method which we call free boundary method. In this approach we ask for scattering solutions at a certain energy ϵ with no assumed boundary conditions. In this case, we introduce an artificial ‘boundary’ at distance R for numerical convenience which causes not any changes neither in the energy eigenvalues of the physical Hamiltonian or in the eigenfunctions themselves.

Considering now again the initial matrix equations (6), we note that we have an non-Hermitian matrix \mathbf{h}_l as well as an overlap matrix \mathbf{U} to be calculated. We ask solutions at certain energy position ϵ , a choice that makes equations (6)

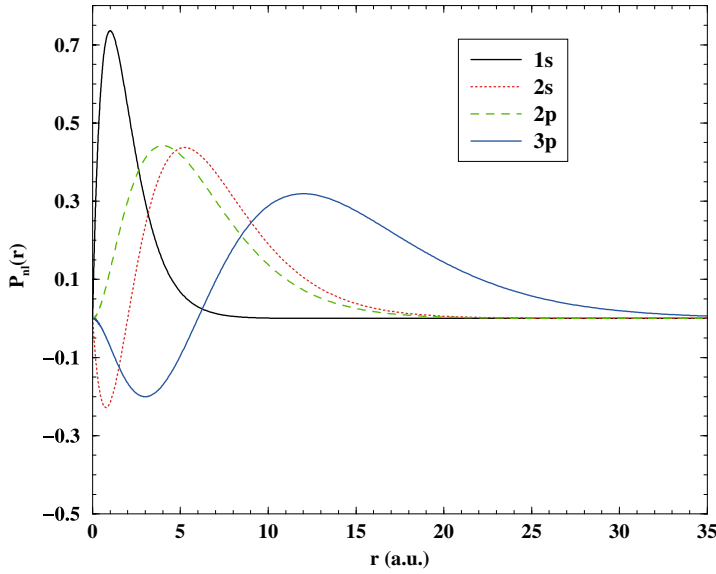


Figure 1. Hydrogen radial bound states.

a system of inhomogeneous linear equations [5]:

$$(\mathbf{h}_l - \epsilon \mathbf{U})\mathbf{C}_{\epsilon l} = 0. \quad (12)$$

At this point we introduce the B-spline polynomials $B_i^{k_s}$ $i = 1, 2, \dots, n_s$, of order k_s , defined in an interval $[0, R]$ on a sequence of knotpoints $t[i] \leq t[i + 1]$, $i = 0, 1, \dots, n_s + k_s$, where $t[0] = t[1] = \dots t[k_s] = 0$ and $t[n_s + 1] = t[n_s + 2] = \dots = t[n_s + k_s] = R$ [6]. In this representation the box-hamiltonian and the overlap matrix elements are given from relations as in equations (7, 8) with the obvious substitution $u_i \rightarrow B_i$ ($U \rightarrow B$). The matrix representation the surface term h^S is given by:

$$h_{ij}^S = -(1/2)B_i(R)B_j'(R). \quad (13)$$

By definition of the B-spline basis, the only non-zero B-splines functions at the boundaries are the first B-spline $B_1(0) = 1$ and the last one $B_{n_s}(R) = 1$. Since the solutions should satisfy $P_{\epsilon/kl}(0) = 0$ we exclude from the basis set the B-spline the first B-spline $B_1(r)$. Furthermore the surface term is reduced to involve only the terms with $i = n_s$. Finally from the properties of B-splines the relations $B_{n_s}'(R) = -B_{n_s-1}'(R) = (k_s - 1)/t_S$, $t_S \equiv t[n_s + 1] - t[n_s]$ are obtained. Then the only non-vanishing elements of the B-splines representation of the Bloch operator are the following:

$$h_{n_s n_s}^S = -h_{n_s n_s-1}^S = \frac{k_s - 1}{t_S} \equiv h_S. \quad (14)$$

This is a clearly unsymmetric matrix since $h_{n_s-1n_s} = 0 \neq h_{n_s n_s-1}$. In the B-spline case, the degree of this non-symmetry can be controlled by varying certain parameters of the basis definition (n_s, k_s) and the knot sequence. It is worth noting that this ‘non-hermiticity’ of the Hamiltonian is independent on the box radius R . It also favors B-spline of lower order k_s . The B-splines Hamiltonian now is given by a non-hermitian matrix of the form:

$$\mathbf{h}_l = \begin{bmatrix} h_{11} & h_{12} & \dots & h_{1(n_s-1)} & h_{1n_s} \\ \dots & \dots & \dots & \dots & \dots \\ h_{(n_s-1)1} & h_{(n_s-1)2} & \dots & \dots & h_{(n_s-1)n_s} \\ h_{n_s1} & h_{n_s2} & \dots & h_{(n_s-1)n_s} + h_S & h_{n_s n_s} \end{bmatrix}. \quad (15)$$

Assuming equations (12) and (15) we rewrite the non-linear system of equations as:

$$(\hat{\mathbf{h}}_l - \epsilon \mathbf{B}) \mathbf{C}_{el} = \mathbf{C}_0, \quad (16)$$

where $\mathbf{C}_0 \equiv (0, 0, \dots, 0, 1)$ and C_{el} are new set of coefficients which related with those of Equation (12), through the relation $C_{el}(\text{new}) = C_{el}(\text{old}) / (h_S C_{n_s-1})$

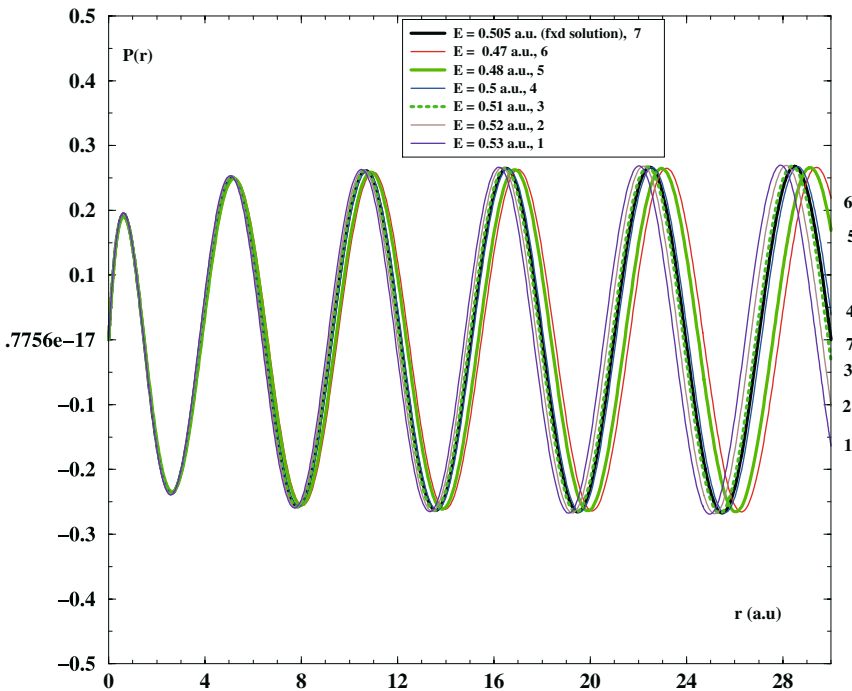


Figure 2. Radial continuum states for different kinetic energies. The box radius was $R = 30$, the number of B-splines $n_s = 92$ and the order was $k_s = 9$. The knot sequence was chosen to be sine-like [4].

(old)). Our effort is to eliminate the problem of non-hermiticity of the box-Hamiltonian. For this, we have rewritten the matrix equations keeping only the hermitian part of the hamiltonian and making the system of linear equations non-homogeneous. The non-Hermitian part of the Hamiltonian, which depends on the product $h_S \cdot C_{n_s-1}$, has been moved to the right-hand side (*RHS*) of those equations, which in principle is *unknown*. Dividing both parts of equations by the *arbitrary* number $h_S \cdot C_{n_s-1}$ we fix the RHS as given by C_0 . This way we have eliminated the problem of non-hermiticity of the box-Hamiltonian with the cost that we are only able to determine a solution vector of arbitrary normalization. The complete determination of the solution vector in the box comes later on, applying the normalization rules that the bound and continuum states should satisfy, according quantum mechanical scattering theory [7].

Normalized continuum states for different kinetic photoelectron energies are shown in figure 2.

4. Normalization of the continuum states (WKB approach)

The procedure, followed for the renormalization of the calculated continuum states, is based to the well known WKB approximation [7]. For a radial SE in a central potential $V_l(r) = -Z_{\text{eff}}/r + u_l(r)$, the normalized solutions, $P(r)$, is known that can be written as:

$$P(r) = \sqrt{\frac{2}{\pi \zeta(r)}} \sin \phi(r), \quad (17)$$

where in the asymptotic region of $P(r \rightarrow \infty)$ the function $\zeta(r)$ satisfies the equation:

$$\zeta^2(r) = w(r) + \zeta^{1/2} \frac{d}{dr} (\zeta^{-1/2}), \quad (18)$$

$$w(r) = k^2/2 - \frac{l(l+1)}{2r^2} - \frac{Z_{\text{eff}}}{r} + u_l(r). \quad (19)$$

The effective charge Z_{eff} is equal to zero ($Z_{\text{eff}} = 0$) for negative ions and unity ($Z_{\text{eff}} = +1$) for neutral atomic systems. The ‘distorted’ potential $u_l(r)$ behaves asymptotically as $u_l(r \rightarrow \infty) \rightarrow 0$. The phase $\phi(r)$ of the wavefunction is given by:

$$\phi(r) = \phi_C(r) + \delta_{kl} = \int_0^{r_0} dr \zeta(r),$$

where we have separated the phase shift into the Coulombing (long-range) (ϕ_C) and the correlation (short-range) (δ_{kl}) part.

Various, similar in spirit, methods have been appeared in the literature, for the solution of the above equations. In our case, we evaluate all the above

equations in the region about $r \rightarrow R$. The numerical calculation of $\zeta(r)$ is performed through a second-order analytical iterative expansion. The details of this expansion is given in the article by Burgess [7].

Being able to calculate the function $\zeta(r)$, we assume that the normalized solution $P_{kl}(r)$ differs by the calculated one $\bar{P}_{kl}(r)$ by a constant in space factor:

$$P_{kl}(r) = A_{kl} \bar{P}_{kl}(r). \quad (20)$$

In the asymptotic region, ($r \sim R$) we force the normalized solution $P_{kl}(r)$ to coincide with the following combination of functions:

$$P_{kl}(r) = a_{kl} F_{kl}(r) + b_{kl} G_{kl}(r), \quad r \rightarrow R, \quad (21)$$

where $F_{kl}(r), G_{kl}(r)$ are the energy-normalized regular and irregular Coulomb functions:

$$F_{kl}(r) = \sqrt{\frac{2}{\pi \zeta(r)}} \sin \phi(r),$$

$$G_{kl}(r) = \sqrt{\frac{2}{\pi \zeta(r)}} \cos \phi(r).$$

Evaluating the equations (17,19,20,21) at the points $r_1, r_2 \sim R$, we find for the short-range phase shift:

$$K_{kl} = \tan \delta_{kl} = \frac{b_{kl}}{a_{kl}} = \frac{\bar{P}_{kl}(r_2)F(r_1) - \bar{P}_{kl}(r_1)F(r_2)}{\bar{P}_{kl}(r_1)G(r_1) - \bar{P}_{kl}(r_2)G(r_1)}. \quad (22)$$

Having calculated the short-range phase shift, we obtain the normalization factor from equations(17,20,22) as:

$$A_{kl} \equiv \frac{\sqrt{2/\pi \zeta(R)} \sin[\phi(R) + \delta_{kl}]}{\bar{P}_{kl}(R)}.$$

The WKB, unnormalized and the normalized radial states for $\epsilon_k = 1.7733$, are shown in figure 3.

At the end of this calculational procedure, we have calculated the two important quantities: (a) the renormalization factor that transforms the calculated wavefunctions to an energy-normalized wavefunctions and (b) the short-range scattering phase shift. The latter is meaningless for the case of hydrogenic one-electron wave functions (always $\delta_{kl} = 0$).

Note that the procedure remains practically the same in the multichannel case. In this case, the outgoing electron moves ($2'$) in the combined central field of the nucleus plus the Coulombing field of the other electron ($1'$). The radial potential $V_l(r)$ is then a non-local potential which its asymptotic limit deviates from the simple electron–nucleus coulombing term Z_{eff}/r_2 by the multipole electron–electron correlation multipoles $v(k; l_1 l_2)/r_{12}^k, k = 1, 2, \dots$

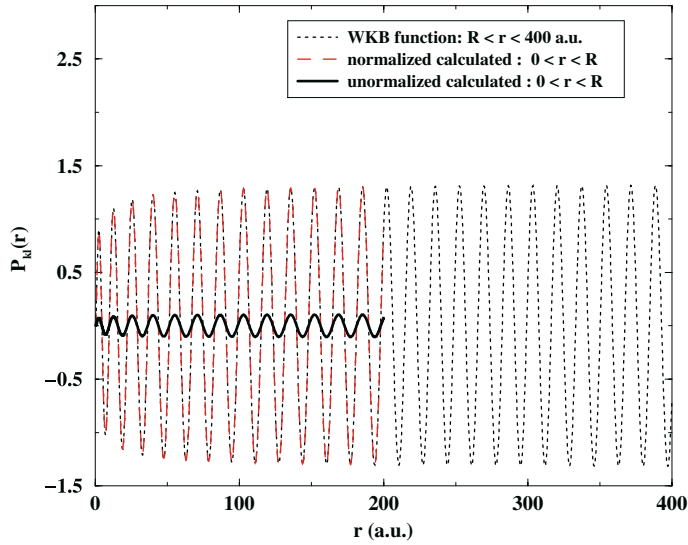


Figure 3. Hydrogen continuum radial state for $l = 1$, $\epsilon_k = 0.06517$ a.u. For $0 < r < R = 200$ a.u. the un-normalized (5) and normalized (20) in energy, radial state is plotted as produced by the calculation. For the region $R < r < 400$ a.u. the WKB asymptotic expansion has been used.

5. Conclusion

In this paper, we have demonstrated the use of the B-splines polynomial basis for the numerical calculation of bound and continuum spectrum of atomic Hamiltonians. Especially for the continuum spectrum, we have employed a method that is able to calculate with high accuracy the eigenstates for a large portion of the space. The method is straightforward extensible to more complex atomic systems having more than one electrons.

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