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ON DIRECTLY SOLVING RADIAL SCHRÖDINGER EQUATION FOR THE GROUND STATES OF TWO ELECTRON ATOMS OR IONS BY GENETIC ALGORITHM

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A recipe is proposed for solving the radial Schrödinger equation (SE) for two electron atoms and ions in their ground states by genetic algorithm (GA). The recipe is tested for the isoelectronic series of H^-, He, Li^+, Be^{2+} atoms and ions. The strong and weak features of the method are analyzed, and possible directions of improvement suggested.

Keywords: Numerical solution of Schrödinger equation, genetic algorithm and SE; GA and solution of radial SE, stochastic solution of SE; helium isoelectronic systems; evolution programming; quantum mechanics.

1. Introduction

A non-conventional way for handling the problem of solving Schrödinger equation (SE) numerically is to cast the task as a complex optimization problem. As a tool, one can then invoke stochastic algorithms like genetic algorithm (GA) for the purpose. The use of GA[1–3] to solve SE numerically is of rather contemporary origin.[4–11] Our own efforts in this area seem to indicate that[5,6,11] GA can be a viable technique for solving SE numerically for many one and two-dimensional systems as well as for the ground and excited states of hydrogen like atoms. The basic philosophy of the method has been to pose the energy-eigenvalue problem in the form of an optimization problem first and then express the targeted solution wave functions as strings representing probability amplitude distribution in the configuration space of the system that undergoes genetic evolution on a properly designed fitness landscape under the action of appropriately designed genetic operators. The amplitudes are floating point numbers and therefore the solution functions are strings of

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floating point numbers. The strings are normalized and made to obey the boundary conditions of the problem.

The results presented in this paper are based on investigations relating to our experimentation on GA-based methods for solving the radial SE for the ground state wave functions of some two electron atoms or ions. A conventional way to handle this problem would be to construct a model helium-like wave function with adjustable parameters, and determine the best wave function within this class by minimizing the energy with respect to the free parameters. The validity and limitations of this method lie in the possibility of constructing better helium-like wave functions that can take care of the electron-nucleus (e-n) as well as electron–electron (e-e) interactions properly. So far, a variety of models have been proposed for constructing correlated wave functions for helium-like systems (for example, see the review by Roothaan and Weiss[12]). In all these cases where one looks for extracting fairly accurate wave functions for multi-electronic systems, the e-e and e-n interactions are treated separately as the trial wave functions are expressed as product of one-electron functions and two particle correlation functions with adjustible parameters. The rest of the job lies in finding the optimum values of those parameters during the optimization of energy. The wave functions obtained here, at any stage of the optimization is separable into corresponding e-n (one-electron functions) and e-e interaction (correlation functions) parts.

In our method each probable solution wave function in the initial population is expressed as a string of floating point numbers[3,5,6] which for the two-electron case represent the probability amplitudes at the designated grid points on the two-dimensional radial grid chosen. Our task is to look for optimal amplitude distribution in the designated configuration space so as to maximize the relevant fitness function. This optimal distribution is achieved through direct adjustment of the amplitudes, brought in by genetic operators, during the evolution of wave function strings under a selection pressure, imposed by the fitness criterion[4–10] based on energy evaluated from wave function strings, numerically. The novelty of our approach lies in the fact that the adjustments in the amplitudes in the configuration space alters e-e and e-n interactions simultaneously. The wave function strings evolve through the generations as inseparable units (not separable in terms of the e-e and e-n correlation parts of the wave function).

2. Method

The SE for the radial part of a spherically symmetric ground state wave function of a two-electron atom reads

$$H\psi_n(r_1, r_2) = E_n\psi_n(r_1, r_2) \tag{1}$$

where

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1}\right) - \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2}\right) - \frac{ze^2}{r_1} - \frac{ze^2}{r_2} + \frac{e^2}{r_{12}}. \tag{2}$$

From the form of the Hamiltonian, it is evident that we are looking at the S-limit situation of the two-electron atomic ground state. The present method can possibly take into account the radial part of the e-e correlation only ignoring the angular part of the correlation altogether.

In the GA-based optimization technique, the first step is the construction of a set of trial wave function strings which make up the initial population; in addition, strings in each generation undergoes three basic operations, "selection", "crossover", "mutation". The modeling of the selection criterion (fitness landscape)[4–10] and the genetic operators (crossover and mutation)[4–10] depends on the nature of the problem posed; however, the basic philosophy[1–3] of these steps remains the same in all the cases. A brief discussion of these elementary steps in GA for two-electron problems considered, is presented in the following subsection.

2.1. *Generation of trial solutions*

We represent ψ on a uniformly discretized two-dimensional coordinate space by strings $(s_1, s_2, \ldots, s_n)$, each string representing a collection of probability amplitudes $[s(i,j)]$ in a two-dimensional array of $n_1 \times n_2$ grid points. The square of the amplitudes $[\{s(i,j)\}^2]$ at a given point (r_1^i, r_2^j) is the probability of finding one-electron at r_1^i while the other is at r_2^j irrespective of spin. The permutation symmetry of the total wavefunction now needs to be considered. Since the ground state is a spin-singlet, the space part of the ground state wave functions of the He- isoelectronic sequence must be symmetric with respect to $1, 2$ interchange. The amplitude distribution in space is therefore constrained to be symmetric under interchange of electronic coordinates. The n different members of probable solutions (wave function strings) are made to interact genetically to generate new sets of strings and thus evolve on the fitness landscape of the problem.

2.2. *Fitness landscape and selection criterion*

We choose an objective function $\mathcal{F}$ in the following form

$$\mathcal{F} = \left\{ \frac{\langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} - E_l \right\}^2 \tag{3}$$

ψ represents one of the n-strings (say s_k) and (E_l) is the approximate lower bound of the ground state energy of the system. Each string contains $n_1 \times n_2$ grid point amplitudes on the two-dimensional radial grid, which are allowed to participate in the genetic evolution, while for evaluation of energy of a given string, in a particular generation, we generate additional number (M) of grid point amplitudes by two-dimensional **bicubic interpolation** and the quadratures are performed over the finer grid that contains all the points $(N + M) \times (N + M)$. The quadratures are straightforward to implement for the one-electron operators. For the two-electron

operator $\left(\frac{1}{r_{12}}\right)$, the integral (I) is represented a follows

$$I = \int \psi^*(r_1, r_2) \frac{1}{r_{12}} \psi(r_1, r_2) \, dv_1 \, dv_2 \tag{4}$$

We proceed by expanding $\frac{1}{r_{12}}$ in terms of the distances r_1 and r_2 of electrons 1 and 2 from the nucleus and the spherical harmonics involving the corresponding angular variables θ_1, ϕ_1, θ_2, ϕ_2. The result is

$$\frac{1}{r_{12}} = \frac{1}{r_1} \sum_{l=0}^{\infty} \sum_{m=1}^{l} \frac{4\pi}{2l+1} \left(\frac{r_2}{r_1}\right)^l Y_{lm}(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) \tag{5}$$

for $r_2 > r_1$, and similarly under exchange of the labels 1 and 2, for $r_2 < r_1$. Noting that we are looking for the ground state wave function for helium atom in the S-limit the integration over the angular variables eliminate all terms from this sum except for $l = m = 0$. The net result is that, inside the integral, we can put $\frac{1}{r_{12}} = \frac{1}{r_1}$ for $r_1 > r_2$ and $\frac{1}{r_2}$ for $r_2 > r_1$ and carry out the required quadratures.

The fitness function (f_k) for the kth string may be defined in different ways. One of these could be

$$f_k = e^{-\sigma \mathcal{F}} \tag{6}$$

while the other takes the form

$$f_k = \frac{\sigma}{\mathcal{F}}. \tag{7}$$

In the first one the value of the fitness function scales between 0 and 1, $(0 < f_k < 1)$ while for the second one the fitness value scales between 0 and ∞, $(0 < f_k < \infty)$. Both the fitness functions are useful depending on the nature of the problem posed. In Eqs. (4) and (5), σ is a parameter that takes care of the dimensional requirements and scale fitness values. After evaluation of fitness values of the set of strings chosen initially, they are subjected to a simple roulette wheel selection procedure[1-3] that allows more copies of the fitter solutions strings to pass into the mating pool. For generation of new strings out of n-members of the mating pool, crossover and mutation operators are applied as described in the following subsection.

2.3. Modeling crossover and mutation operators

A typical string, say, S_k is a two-dimensional array with a unique value assigned to each element of the array, with $i = 1, n_1$; $j = 1, n_2$. If S_k and S_l are randomly chosen strings from the mating pool, for crossover with probability p_c, and the crossover site is the ith row and jth column, then a pair of new strings can be generated by the following transformations[5,6]:

$$S'_k(p, q) = f S_k(p, q) + (1 - f) S_l(p, q) \tag{8}$$

$$S'_l(p, q) = f S_l(p, q) + (1 - f) S_k(p, q) \tag{9}$$

for $p = i + 1, n_1$; $q = j + 1, n_2$, while for $p \leq i, q \leq j$,

$$S_k'(p, q) = S_k(p, q) \tag{10}$$

$$S_l'(p, q) = S_l(p, q) \tag{11}$$

The mixing weight $f (0 < f < 1)$ is randomly chosen from a given range of values.

After crossover each member is subjected to mutational transformation[5,6] with mutation probability p_m as follows:

$$S_k''(p, q) = S_k'(p, q) + (-1)^l r \cdot \Delta_m \tag{12}$$

where r is a random number ($0 \leq r \leq 1$), l is random integer and Δ_m is the mutation intensity which may be kept fixed or changed from generation to generation. The mutation probability (p_m) is kept constant throughout the generations and is usually a small number (0.05–0.04).

Keeping in view the fact that the radial part of the ground state two-electron wave function would be spatially symmetric under interchange of electron labels, we use an additional operation on the post-crossover and post-mutation strings. This is the symmetrization of the radial wave function as follows:

$$S_k'''(q, p) = S_k''(p, q) \tag{13}$$

for $p = 1, n$; $q = p, n$ and $k = 1, npop$; where "npop" is the number of strings in the population.

From the post-symmetrized population, 80% of the strings were chosen according to their fitness and the remaining 20% were chosen randomly. The entire sequence of four operations (selection, crossover, mutation and symmetrization) constitute one generation and is repeated until the fitness distribution in the population approaches a δ function.

3. Results and Discussion

The method outlined for solving SE for the radial part of a spherically symmetric wave function for the ground state of two-electron atoms have been applied to the helium isoelectronic series H^-, He, Li^+, Be^{2+}. ψ has been represented as an amplitude distribution function on a grid of length 20 a.u. in each dimension while each dimension contained 500 grid points. Each string thus carried 500×500 grid point amplitudes during evolution while the quadratures were performed over $1{,}500 \times 1{,}500$ grid point amplitudes for more accurate evaluation of the energy, *the extra amplitudes being generated by two-dimensional bicubic interpolation*. A population size of 10 was used uniformly for all the cases. No attempt has been made to optimize the GA parameters.

The trial set of solutions in the initial population were chosen by constructing spatial distribution of amplitudes on the two-dimensional radial grid from two types

of functions:

(i) Model correlated wave function of the closed-shell type[12]

$$\psi_{\text{trial}} = Ne^{-\alpha(r_1+r_2)}\chi(r_{12}) \tag{14}$$

$\chi(r_{12})$ is the correlation function $(1 + \gamma r_{12} + \cdots)$, and α and γ are a randomly chosen parameters.

(ii) Product of two one-electron functions of the closed-shell type[12];

$$\psi_{\text{trial}} = Ne^{-\beta(r_1+r_2)}. \tag{15}$$

We choose the variationally optimized value[3] of β, for one of the ten trial solutions in the initial population while the others were chosen randomly.

Our idea has been to test whether the information content in the trial set of solutions (made up of randomly chosen two-electron correlated wave functions as well as uncorrelated functions) could be exploited by the genetic operators to make the strings evolve into the best possible ground state wave function of the radial SE within the approximation level used.

After the selection phase is over a pair of strings were chosen from the selected strings (with crossover probability $p_c = 0.75$) for the crossover operations, which is implemented following the CO scheme mentioned in the Sec. C viz. Eqs. (6) and (7) with the difference that the indices p and q in those equations run from 1 to i and 1 to j, respectively (instead of $p = i+1, n_1$; $q = j+1, n_2$), while for Eqs. (8) and (9), the indices p and q run from $i+1$ to n_1 and $j+1$ to n_2 respectively (instead of $p = 1$, i; $q = 1, j$), where the crossover site is the ith row and jth column of a string. This modified CO scheme allows the algorithm to explore the most important region of space (closer to the nucleus) more efficiently and has been found to improve the performance of the algorithm in a preliminary applications.[6,14]

The post-crossover strings were subjected to mutation with a probability $p_m = 0.05$ following the scheme mentioned in Sec. 2.3, Eq. (12) and subsequently symmetrized.

Table 1 displays the ground state energy of the isoelectronic atoms/ions corresponding to the best wave function string in converged solution pool. It is clear

Table 1. Comparison of ground state energies predicted by the GA-driven method and the CI method. Hartree–Fock energies are also included for reference.

State and Atom Designation	Energy Predicted by the Hartree–Fock Method[a] (a.u.)	Energy Predicted by the the GA-Driven Method (a.u.)	S-Limit Energies Obtained from CI Calculations[b] (a.u.)
$^1S_0$, He	−2.86168	−2.87505	−2.87902
$^1S_0$, Li$^+$	−7.23641	−7.24799	−7.25249
$^1S_0$, Be^{+2}	−13.61113	−13.62049	−13.62685
$^1S_0$, H$^-$	−0.48793	−0.51198	−0.51449

[a]Roothaan and Weiss[12]; [b]Davis.[13]

that the energies obtained are slightly better than the corresponding Hartree–Fock energies[14] while being slightly inferior to the S-limit energy obtained from CI calculation,[13] suggesting that only a part of the radial correlation has been incorporated. Longer evolution over a denser grid of points close to the nucleus appears to be needed for higher accuracy. The general pattern of performance of the proposed methodology can be assessed from the evolution profiles for a few representative cases.

Figures 1(a) and (b) show the energy profiles during the evolution of the best fit string in each generation during the GA-based search for the ground state energy and wave function of He and Li^+ while Figs. 1(c) and (d) show the same profiles for Be^{2+} and H^- ions. Our GA-based search leads to the S-limit ground state energy of these two-electron systems fairly closely, as seen from comparison with the previously reported results.[13]

The rapid improvement in the energy at the initial stages of evolution is an attribute of the modified crossover scheme that ensures more frequent sampling of most important region of space contributing to the energy of the ground state of two-electron atoms or ions, during the crossover (exchange of information) operation. At the later stage of the evolution the optimization is mainly mutation driven when only minor corrections are introduced in the wave function by the mutation operator leading to a slow improvement of energy. The fitness profile for the GA optimization of Be^{2+} ion is shown in Fig. 2. The explanation for the rapid improvement of fitness in the earlier stage and rather slow fitness increment in the latter stage of the evolution is the same as that for the trend of energy evolution.
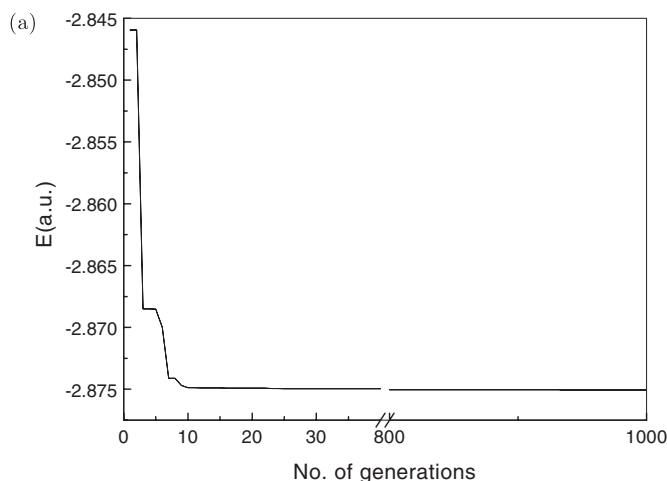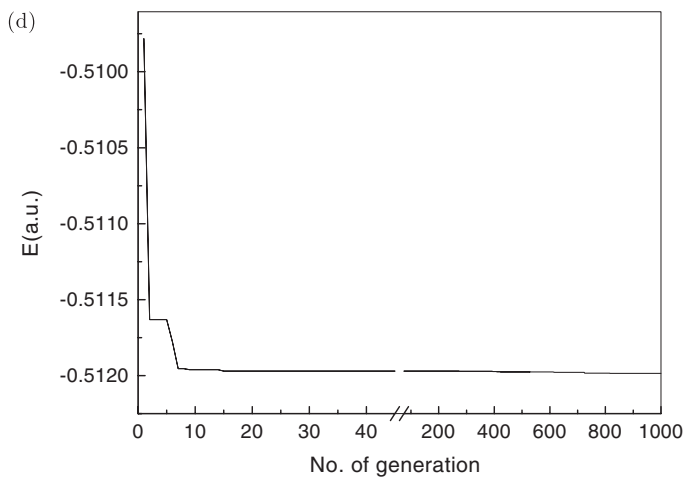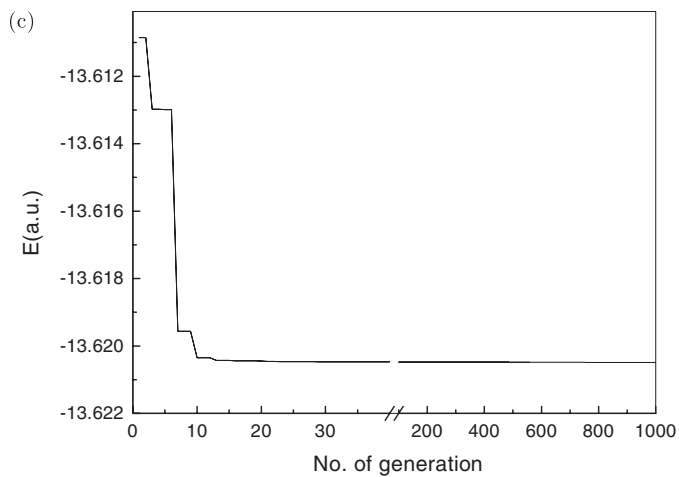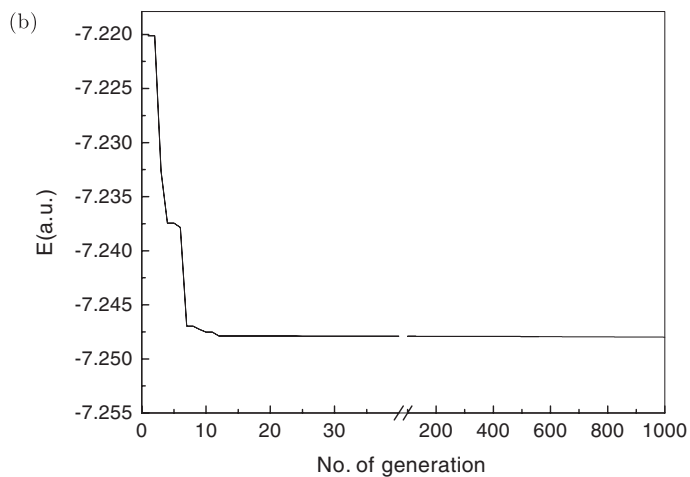

Fig. 1. Evolution of energy for the ground state of the He-isoelectronic series during the GA run. The energy refers to the string of the highest fitness in the population. (a) He atom; (b) Li^+ ion; (c) Be^{2+} ion; (d) H^- ion.
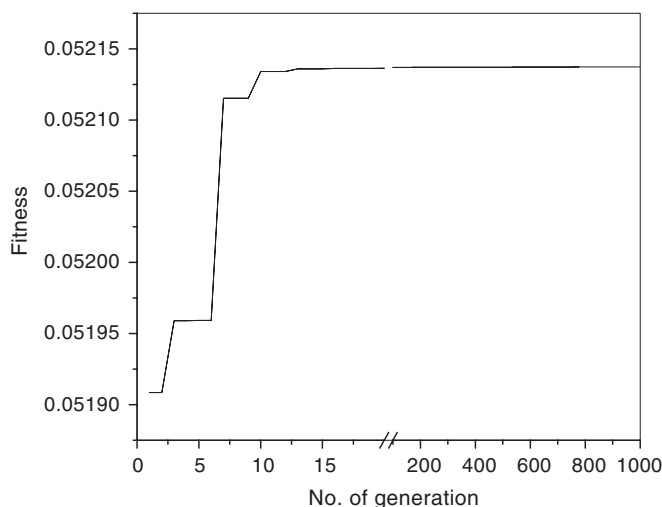
(b)

(c)

(d)

Fig. 1. (*Continued*)

Fig. 2. The fitness profile during the GA run for the Be^{2+} ion in the ground state. The fitness corresponds to the string of the highest fitness in any generation.

From the two-dimensional contour plots of the wave function amplitudes for the isoelectronic series Be^{2+}, Li^+, He, H^- shown in Figs. 3(a)–(d), one may note that the probability of finding the electrons in the region of space where $r_1 = r_2$ decreases significantly from Be^{2+} to H^- in the isoelectronic series. This is in agreement with the fact that, the electron–electron correlation increases from Be^{2+} to H^- in the series while electron-nuclear correlation decreases from Be^{2+} to H^- due to the decrease of nuclear charge in that direction in the series. As representative examples, we have shown in Figs. 4(a) and (b), the probability plotted as functions of radial coordinates (r_1, r_2) for the Be^{2+} and H^- ions, respectively. From these figures, the highly contracted nature of the wave function for the Be^{2+} ground state is as much evident as the rather diffuse nature of the wave function for the H^- ground state. The nature of the wave function has an important bearing on the practical implementation of genetic algorithm driven solution of SE. Due to the highly contracted nature of the Be^{2+} wave function one is forced to choose a relatively much larger number of grid point amplitudes in the region of space near the nucleus for they contribute more to the energy of the system. One way to tackle this situation is to take a non-uniform distribution of grid points over a given grid length, with larger number of grid points being used in the region near the nucleus. The other way could be to shorten the grid length keeping the uniform distribution of grid points intact (as in the He one). We have chosen the second option in this case as the implementation of quadratures is cumbersome on a non-uniform grid.

For H^- the radial wave function is a highly diffuse one. In this case, amplitudes at grid points far away from the nucleus still contribute significantly to the energy of the system. So one has to choose a relatively broader distribution of grid points.
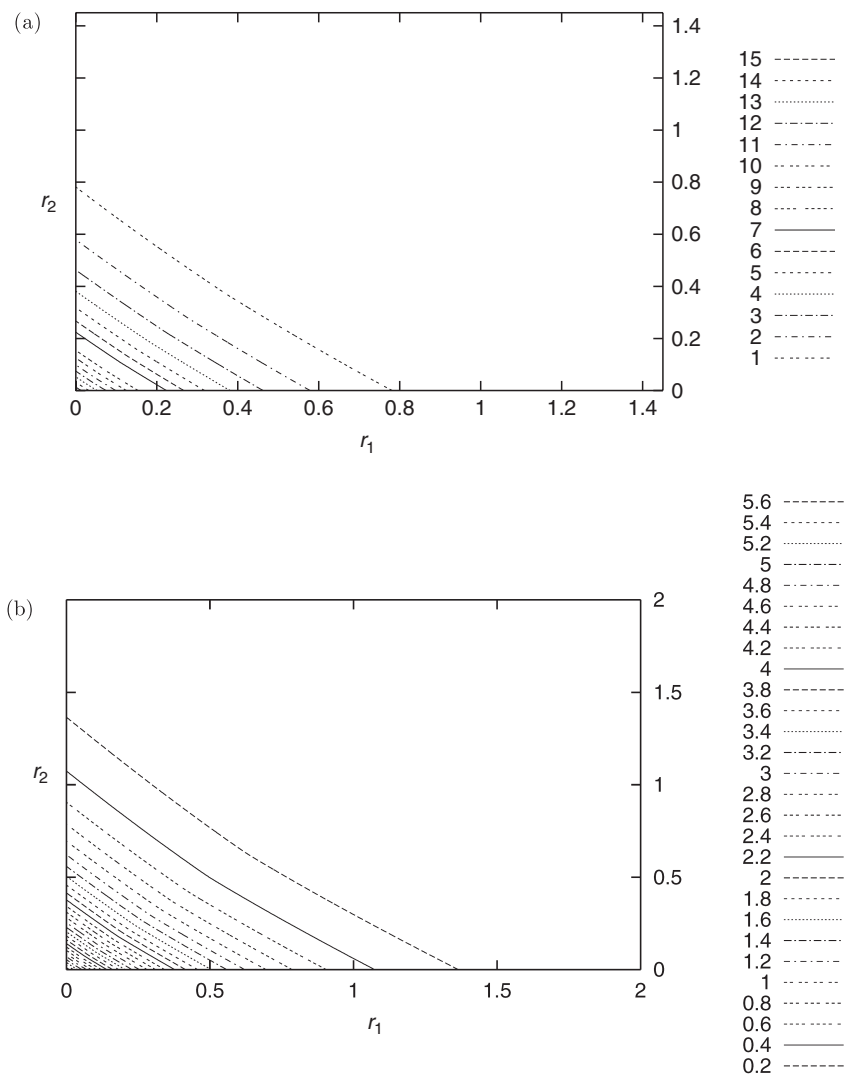
Fig. 3. The two-dimensional contour plots of wave function amplitudes for the isoelectronic series in their ground state. (a) Be^{2+} ion; (b) Li^+ ion; (c) He atom; (d) H^- ion.

A uniform distribution of grid points taken over grid length of 20 a.u. in each dimension served the purpose well. An additional difficulty in this case is that the fitness landscape is much more rough and rugged and has many peaks at different heights. So one must design genetic operators in such a fashion that the population is able to hop from one hill to another and avoid getting stuck on a local maxima on the fitness landscape. We are exploring the possibility of using a non-uniform grid and an annealed GA in the present context. A strong feature of the method lies in its ability to quickly explore the search space and produce a few good strings.
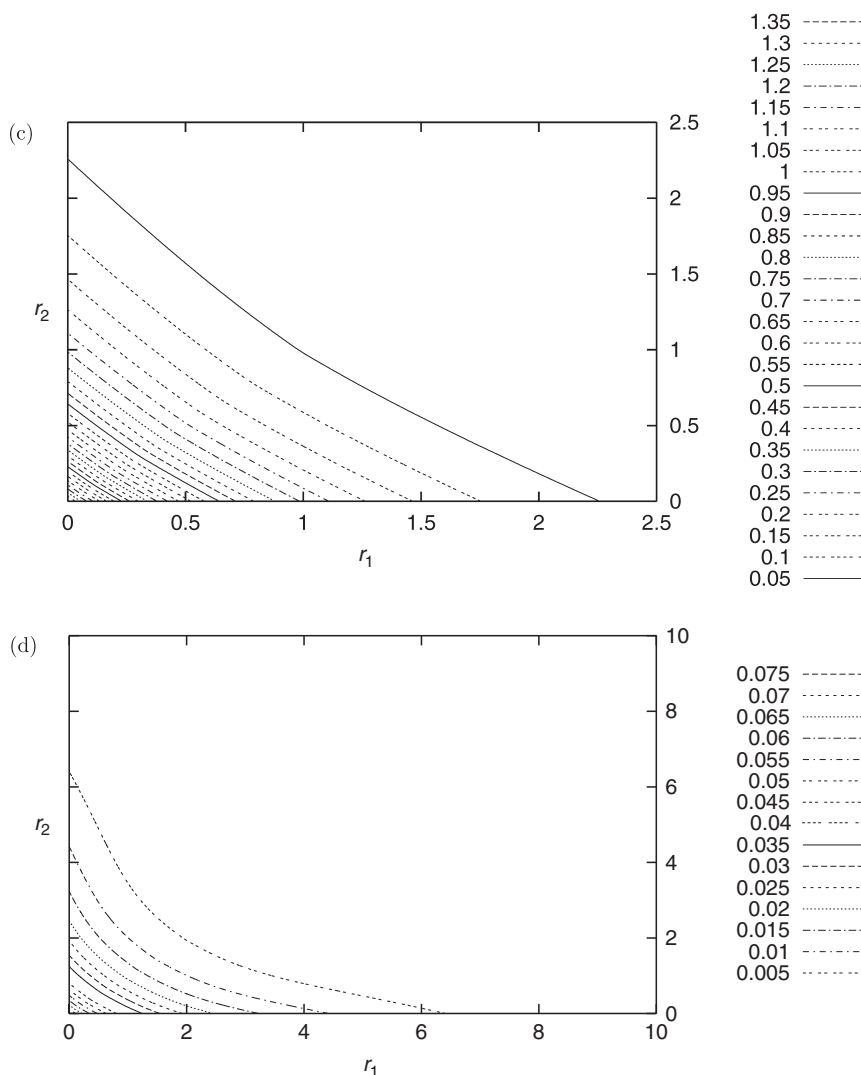
Fig. 3. (*Continued*)

The higher the volume of information present in the search space to start with, the quicker is the climb to a local maxima on the fitness landscape. An adequate number of strings with widely distributed fitness values are therefore necessary. We note here that due to hardware constraints (Pentium-III @ 350 MHz has been used) we have used only ten strings in the population while approximately twenty would perhaps have been optimal. Parallelization of the code would go a long way in solving these problems. Our experience with implementation of parallel GA-based method of solving SE one- and two-dimensional systems[11] indicates that it would be essential for cost-effective GA-based approach to multi-dimensional problems.
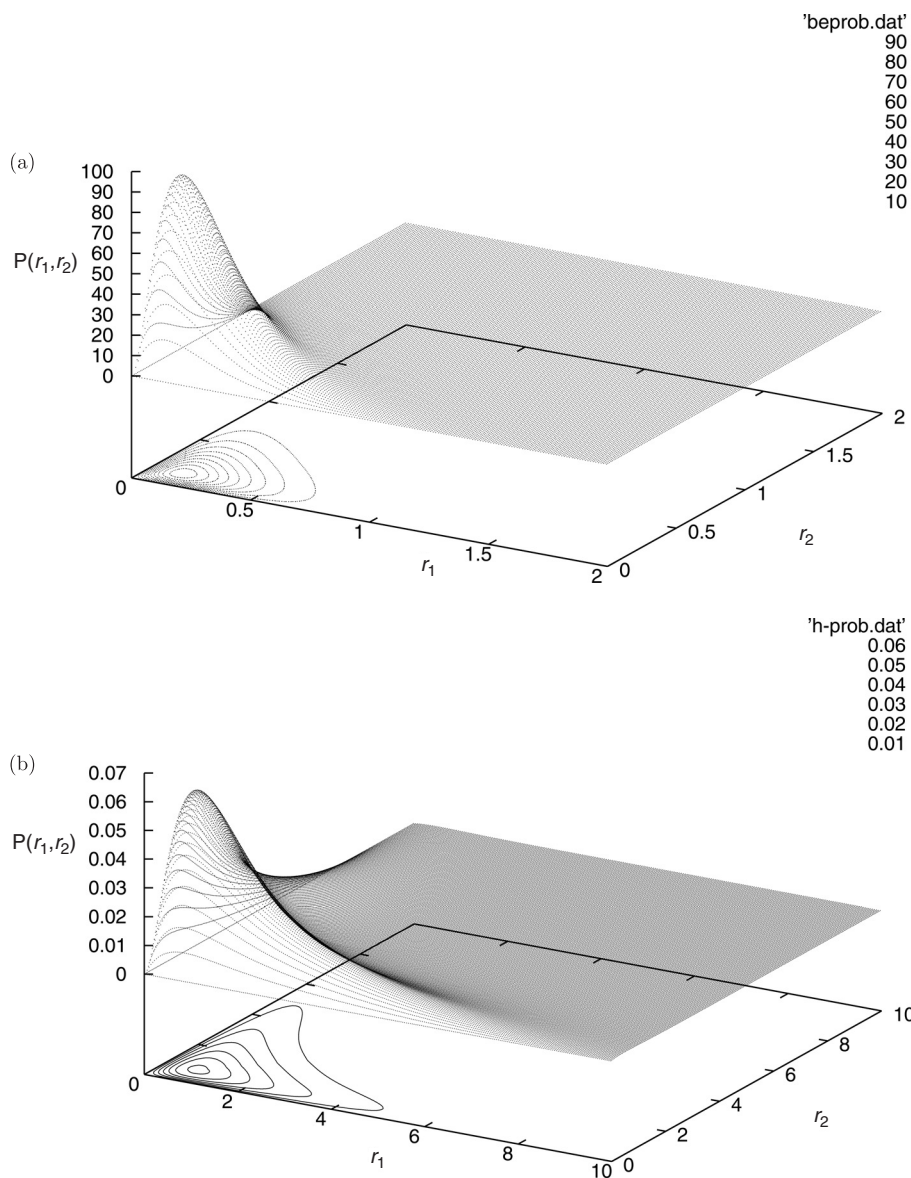
Fig. 4. The ground state probability ($P(r_1, r_2)$) distribution plotted as a function of the radial coordinates r_1 and r_2. (a) Be^{2+} ion; (b) H^- ion.

4. Conclusions

The performance of our GA-based approach to solve the radial SE for ground state ($^1S_0$) of two-electron atoms is encouraging. The extension of the method to obtain the complete wave function for multi-electronic system turns out to be computationally costly as one has to perform multi-dimensional quadratures in such cases.

We are presently evaluating usefulness of the Monte Carlo technique for the multi-dimensional quadratures instead of trapezoid or Simpson's rule based quadratures in place. To overcome the problem, at present. It appears that parallelization of the code is necessary to reduce the computational cost as we go for solving higher-dimensional systems. Our preliminary explorations[11] with single electron atoms or two-dimensional oscillators have shown that parallelization leads to a remarkable gain in efficiency of the GA driven algorithms. We hope to return to the problem in near future.

Acknowledgments

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