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Direct solution of Schrödinger equation by genetic algorithm: test cases

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Abstract

A stable and generalizable recipe is proposed for directly solving Schrödinger equation by genetic algorithm. The recipe is tested for obtaining (i) the radial wave function of the H-atom in the ground and excited states, (ii) ground and excited states in a symmetric double well potential, (iii) ground and excited states of two coupled harmonic oscillators. The possibility of generalising and extending the recipe to more complex problems is analysed. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The techniques of electronic structure calculation have made progress in the past decade to such an extent that experimentalists have started using available quantum chemistry packages for a variety of purposes. Fairly accurate calculations on medium sized molecules are now routinely done if computers with appropriate hardware capabilities are available. These techniques (ab initio SCF-MO, CI, MRD-CI, MC-SCF, coupled cluster, etc.) [1–3] now in use have been perfected over the years and continuous refinements are still taking place. In such calculations one is constrained to make use of a basis set that the available hardware can support. There have been attempts to design optimal basis sets, but the task of finding optimal sets for every atom in every chemical environment and for every property is a formidable one. Useful input to the basis set designing problem can come from detailed knowledge about the stationary states that the Schrödinger equation (SE) predicts for simple atoms and molecules specially in the most important regions of space. The information can be exploited to design analytical basis sets for different atoms in different chemical environments. One may be keen therefore to look for numerical solution of the SE for low-dimensional systems—namely, atoms and diatoms with a few electrons and nuclei.

The task of numerically solving the SE is a difficult one. The standard routes involving numerical integration of differential equation or their finite difference transcriptions have been explored with some success. Search for alternative techniques of handling the problem is still on. One such alternative may be to cast the problem in the mould of an optimization task and then invoke the powerful artificial intelligence (AI) methods to solve it. A search of literature reveals that the genetic algorithm (GA), a power-

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ful global optimizer [4–6] has been recently explored [7–13] in this context. The explorations have taken off in two distinct directions. While Markov and Metiu [12] have used genetic programming which searches out the optimal form of the unknown solution from a database of a variety of elementary candidate functions, Choudhury and Bhattacharyya [8] have experimented with genetic evolution of floating point strings representing possible probability amplitude distributions in the configuration space. A salient feature of the latter method has been the use of a simple arithmetic single site crossover mechanism on floating point strings and a similar scheme for mutation, for generating new strings. Others too have used similar schemes [11–14]. In the present communication we describe a more generalised version of our previously reported [8] GA based recipe and present results of our exploration with it in extracting stationary solutions of Schrödinger equation for simple, but non-trivial systems and indicate how it can be possibly invoked for more complex systems. The present algorithm differs from the previous one reported by us [8] in (i) the use of interpolation to generate amplitude distribution on a finer grid for performing quadratures while the evolution occurs on a coarse one; (ii) the introduction of new crossover schemes some of which depend upon the nature of the potential; (iii) the use of a dynamic mutation scheme; (iv) the ability of the algorithm to handle constraints by using a modified objective function.

It turns out that (i), (ii) and (iii) lead to a very significant improvement in the performance of the algorithm (see later) and (iv) enables the algorithm to look for excited states.

2. Method

Let us consider the SE in one dimension

$$H\psi(x) = E\psi(x). \tag{1}$$

We present Ψ in a uniformly discretized coordinate space by strings $(S_1, S_2, S_3, \ldots, S_n)$, each string representing a collection of probability amplitudes $(a_1, a_2, \ldots, a_n)$ at the designated points $(x_1, x_2, \ldots, x_n)$ in the coordinate space. Notationally, we have

$$\begin{aligned} S_1 &\equiv S\big(\psi_1(x_1), \psi_1(x_2), \ldots, \psi_1(x_k), \ldots, \psi_1(x_n)\big),\\ S_2 &\equiv S\big(\psi_2(x_1), \psi_2(x_2), \ldots, \psi_2(x_k), \ldots, \psi_2(x_n)\big),\\ &\vdots\\ S_m &\equiv S\big(\psi_m(x_1), \psi_m(x_2), \ldots, \psi_m(x_k), \ldots, \psi_m(x_n)\big). \end{aligned} \tag{2}$$

The probability amplitudes in each string are selected randomly under the constraint that they conform to the requirements of the boundary conditions of the problem and nodal characteristics of the wave function being sought. Thus, for the ground state we demand that $\psi(x_k) \to 0$ as $x_k \to \infty$ and each of the strings $(S_1, S_2, S_3, \ldots, S_n)$ describe a probability amplitude distribution that is nodeless. Once the strings are defined and made, we have to construct an objective function that serves as the generator of fitness for every string in the given population. Maximization of the fitness values of the strings in the population will be the goal of the search implying that achievement of maximal fitness would amount to extracting the true solution of the wave equation. The process would mimic in a way the Darwinian tenet of the survival of the fittest.

2.1. The ground state problem

A simple and elegant choice of the objective function $\mathcal{F}$ for the ground state is

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

where E_l is an estimated lower bound to the energy functional. E_l can be updated at any stage, if required. For the ith string in the population we have

$$\begin{aligned} \mathcal{F}_i &= \left[\frac{\langle\psi_i|H|\psi_i\rangle}{\langle\psi_i|\psi_i\rangle} - E_l \right]^2\\ &\equiv \left[\frac{\langle S_i|H|S_i\rangle^s}{\langle S_i|S_i\rangle^s} - E_l \right]^2. \end{aligned} \tag{4}$$

$\langle\ \rangle^s$ indicates that the integration has been replaced by quadratures over the points at which amplitudes are known for the string in question. At this point we make an important departure from the scheme described in our previous publication [8]. In the present method, while *only the n-grid point amplitudes are allowed to participate in the genetic evolution, we carry out cubic spline/bicubic interpolations to generate amplitudes at additional points between each pair of grid points* and

the quadratures are performed over the finer grid that contains all the points, direct as well as interpolated.

Let us assume that the implied integrations have been carried out in the discretized space by a suitable quadrature. The $\mathcal{F}_i$ values are then mapped into a corresponding series of fitness values by defining the fitness f_i as

$$f_i = e^{-\sigma \mathcal{F}_i}, \tag{5}$$

where σ is a constant of appropriate dimension. One can easily see that $f_i \to 1$ as $\mathcal{F}_i \to 0$, while $\mathcal{F}_i \to 0$ as $\langle S_i|H|S_i\rangle/\langle S_i|S_i\rangle \to E_l$.

The fitness criterion of Eq. (5) is energy based. Since the energy is always estimated with an accuracy that is one order higher than the accuracy of the wave function one may be keen to learn about the accuracy of the evolving wave function. It would be good to define another fitness parameter f_i^* as

$$f_i^* = e^{-\sigma \mathcal{G}_i}, \tag{6}$$

where $G_i = ||(H - E_i)\psi_i||$ and $||\ ||$ defines the norm of the vector $|(H - E_i)\psi_i\rangle$. Since the norm of the error vector would be large to start with, it is advisable to start with $f_i = e^{\sigma \mathcal{F}_i}$ and switch over to f_i^* only at a latter stage, set $\sigma = 1$ and look for the limit $f_i^* \to 1$.

When the appropriate limits are reached, one may assume to have obtained the solution. The initially chosen population is made to undergo a simulated evolution for many generations, each generation comprising in selection, crossover and mutation processes. We employ a fitness proportional mechanism of selection based on the slotted roulette wheel [5]. For introducing new strings two strings are allowed to interact with partial exchange of information (crossover) and each of the strings is then made to undergo an environment induced type of random changes of small amplitudes (mutation). The process of crossover is allowed to occur with a preset probability ($p_c < 1$). Let us suppose that a pair of strings S_i and S_j are selected for crossover randomly and that the crossover site has been randomly chosen to be the kth site. We define the operation as follows:

$$S_i \oplus S_j \Rightarrow S_i' \oplus S_j', \tag{7}$$

where

$$\begin{aligned} S_i' &= S\big(\psi_i(x_1), \psi_i(x_2), \ldots, \psi_i'(x_k), \ldots, \psi_i'(x_n)\big), \\ S_j' &= S\big(\psi_j(x_1), \psi_j(x_2), \ldots, \psi_j'(x_k), \ldots, \psi_j'(x_n)\big), \end{aligned} \tag{8}$$

and

$$\begin{aligned} &\psi_i'(x_l) = f\psi_i(x_l) + (1-f)\psi_j(x_l), \\ &\psi_j'(x_l) = (1-f)\psi_i(x_l) + f\psi_j(x_l), \\ &\quad \text{for } l = k, k+1, \ldots, n, \end{aligned} \tag{9}$$

f here being a number in the range $0 < f < 1$, chosen randomly from a Gaussian distribution. Crossover thus creates new amplitude distributions in the form of new strings. We note here that the present scheme of crossover introduces much larger changes in the wave function in a single operation compared to the scheme defined in Ref. [8]. The pre-crossover strings are called parents and post-crossover new strings are called offsprings. In addition to the single point crossover, we have kept options for a multisite crossover scheme in which more than one sites (say the kth, lth, and mth) may be chosen simultaneously for crossover. In this case the amplitudes at the selected grid points only, i.e., $\psi_i(x_k), \psi_i(x_l), \psi_i(x_m)$ are allowed to undergo the mixings defined in Eqs. (9). It turns out that the best crossover scheme in a given potential may depend upon its nature and different potential-dependent crossover schemes may have to be adopted in some cases (see Section 3).

We retain both the n parents and the n offsprings in two separate pools after crossover. Each of the n members of the post-crossover population of the offsprings is made to undergo the process of mutation with a probability $p_m \ll 1$ (0.0009–0.05) and an intensity $\Delta \ll 1$ (0.00001–0.015). For each string, all the m sites are scanned by generating a random number r ($0 < r < 1$) for all the sites. The site (let us say the kth) for which $r < p_m$ (0.0009–0.01), the corresponding amplitude (kth amplitude of the ith string) is made to undergo mutation. For simulating mutation, we have adopted three different models:

(a) *Constant mutation intensity model*. This model was used in our previous paper [8] where the mutated string is defined as

$$\Psi_i'(x_k) \Rightarrow \Psi_i''(x_k) = \Psi_i'(x_k) + (-1)^L r\Delta, \tag{10}$$

where L is a random integer, r is a random number ($0 < r < 1$) and Δ is a mutation intensity factor chosen from a given range. *To prevent unwanted kinks in the wave function* [10], *we keep the mutation intensity proportional to the amplitude being mutated*.

(b) *Variable mutation intensity models.* (i) Δ is assumed to be inversely proportional to the number of generation elapsed (n_g):

$$\Delta(n_g) = \Delta_0 \frac{1}{n_g}, \tag{11}$$

where Δ_0 is the initial intensity of mutation. (ii) Δ is assumed to be a continuously changing function of n_g. The specific form chosen in the present calculation is

$$\Delta(n_g, y) = y\left[1 - r^{(1-n_g/T)^l}\right], \tag{12}$$

where r is a random number in the range $0 \leqslant r \leqslant 1$, T is the maximum number of generations during which the evolution would take place, l is a system-dependent parameter ($l = 2$ has been used) while y is chosen from specified range ($b_{\min} \leqslant y \leqslant b_{\max}$) [6]. When the parameters are chosen in this manner $\Delta \to 0$ as $n_g \to T$.

After the crossover and mutation operations are over, each modified string is normalized and used for fresh evaluation of the energy integral and fitness parameter and subjected to the selection process together with the n parents from the past generation. As generations elapse, the fitness distribution in the population approaches a delta function like distribution with $f^{\text{best}} \to 1$. The amplitudes coded by the best strings in the population and the corresponding energy value are taken to represent the ground state wave function and energy.

2.2. Excited states

For the first excited state (ϕ) the general sequence of operations remains the same with two modifications: (i) the initial strings are so chosen as to ensure the presence of only one node in each; (ii) the objective function now has an additional term to take care of the orthogonality requirement $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle = 0$. The modified objective function $\tilde{\mathcal{F}}$ is defined as follows:

$$\tilde{\mathcal{F}} = \left\{\frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} - E_l\right\}^2 + \beta\left|\langle\psi|\phi\rangle\right|^2. \tag{13}$$

In Eq. (13) ψ is the ground state wave function already calculated, and β is a penalty weight factor of appropriate dimension. The higher excited states can be determined sequentially. For the nth state $n-1$ orthogonality constraints are to be imposed. One can do away with the explicit penalty term in the objective function arising out of orthogonality constraint by making each string in the population orthogonal to the lower exact eigenstate at every generation (a procedure previously used by us). The lower bound estimate (E_l) in Eqs. (3) or (13) is the last parameter that needs to be specified. It is best to use a small basis and diagonalize the Hamiltonian directly or perturbatively to get an approximate estimate of E_l which should be lower than the approximately estimated lowest eigenvalue of the concerned Hamiltonian. At any stage of evolution, E_l may be redefined ($E_l \to E_l \pm \sigma$), if needed.

3. Results and discussion

We have applied the methodology outlined in the previous section to the (a) determination of the ground and excited state wave functions and energies in a symmetric double well potential; (b) determination of the ground and excited states of hydrogen atom; (c) determination of the ground and excited states in a two-dimensional coupled harmonic oscillator.

3.1. The symmetric double well problem

The Hamiltonian describing the system is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + 0.01x^4 - 0.02x^2 \quad (m = 1836). \tag{14}$$

The GA calculations were done with a population of size 20. Initially each individual string was generated randomly by generating a total of 123 probability amplitudes at 123 grid points defining the string. Single point crossover (Eqs. (8)) together with fixed crossover probability $p_c = 0.25$ and a constant mutation (Eq. (10)) rate and intensity ($p_m = 0.05$, $\Delta = 0.015$) were used. Many different types of selection procedure [6] exist, but we have adopted the standard roulette wheel procedure [5,6]. We have explicitly used 123 grid points and therefore only 123 grid points amplitudes of Ψ were explicitly used in the GA based evolution. That is, each of the strings or chromosomes had 123 genes. However, to improve the quality of quadratures (trapezoid rule is used throughout) we have used the cubic spline interpolation to generate a eight additional amplitudes between each pair of grid

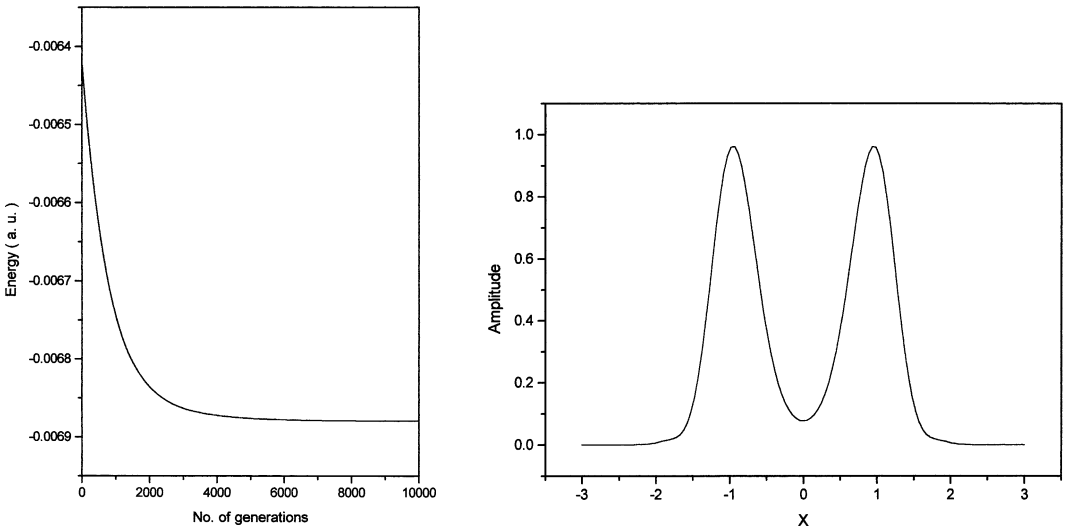


Fig. 1. (a) Evolution of energy for the ground state of the system with double well potential during the GA run. The energy refers to the string of the highest fitness in the population. (b) The plot of GA optimized ground state wave function for the system with double well potential.

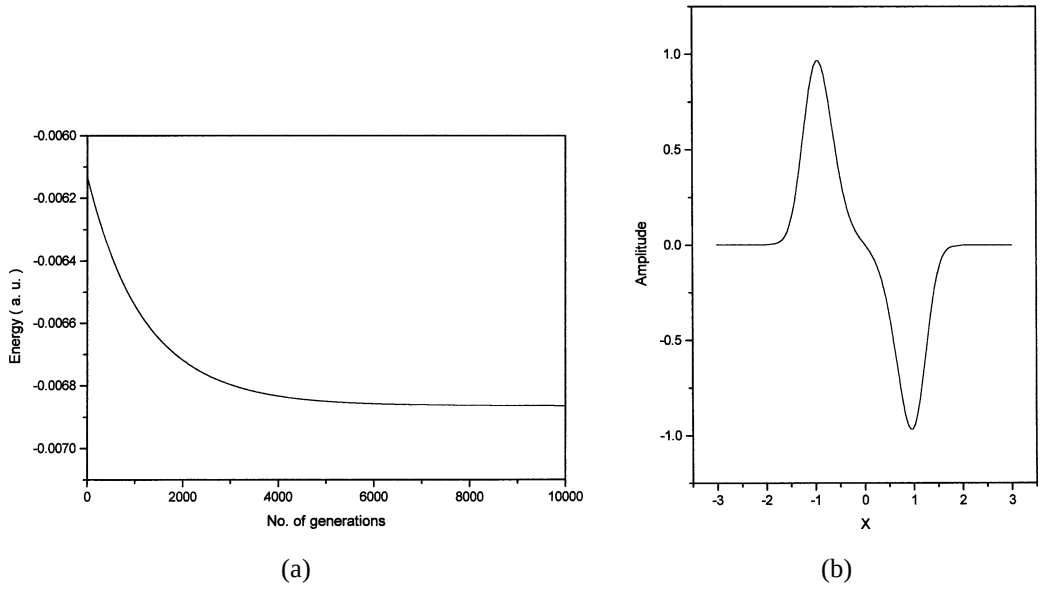


Fig. 2. (a) Evolution of energy for the first excited state of the system with double well potential during the GA run. (b) The plot of GA optimized first excited state wave function for the system with double well potential.

points for every string. The improved quadratures lead to a smooth evolution and the quality of wave function and energy improve to the desired level of accuracy.

During the evolution the energy of the best fit individual decreased gradually. The energy profile is shown in Fig. 1(a). There is a long tail in the energy

profile which is reproduced here to emphasize that there was virtually no improvement beyond the 6000th generation signaling that it is not a case of premature convergence. The amplitudes encoded by the best individual in the population at convergence have been shown as the computed ground state wave function in Fig. 1(b).

For calculating the first excited state Ψ_1, Ψ_0 of Fig. 1(b) was used for imposing the orthogonality constraint $\langle\psi_0|\psi_1\rangle = 0$. In any particular generation all the individual one node strings in the population were Schmidt orthogonalized to the ground state (ψ_0) determined in the first step (β in Eq. (13) accordingly set equal to zero). Fig. 2(a) displays the energy profile of the best string during the evolution. The wave function corresponding to the best string in the converged population computed by us is shown in Fig. 2(b). For both the states, energy and wave function were also computed by the FGH method [13] for comparison. The two sets of results showed excellent agreement (for energy $E_1 = -0.00687$ a.u. in the FGH calculation, versus -0.00686 a.u. in the GA based one).

3.2. The H-atom problem

Since the SE here is separable in spherical polar coordinates, we consider only the radial Schrödinger equation for the H-atom. The equation reads

$$-\frac{\hbar^2}{2m}\left[\frac{\delta^2\psi}{\delta r^2} + \frac{2}{r}\frac{\delta\psi}{\delta r}\right] - \left(\frac{e^2}{r} - E\right)\psi = 0. \qquad (15)$$

Ψ has been represented as an amplitude distribution at designated grid points ($r_i = 0, \ldots, 25$ a.u.). Each string thus carried 200 grid point amplitudes explicitly while the quadratures are performed over 2000 grid points, the extra amplitude being generated by cubic spline interpolation. A population size of 20 was used.

Figs. 3(a) and (b) compare the computed energy evolution profiles of the H-atom in the ground state for the single point arithmetic crossover and multisite arithmetic crossover schemes, respectively (mutation probability and intensity were held fixed). From the figures ($p_m = 0.05$ and $\Delta = 0.0015$) we tend to conclude that the two crossover schemes (single and multisite) introduced here virtually lead to identical convergence profiles. Fig. 3(c), on the other hand, represents the convergence profile when a modified single point crossover (CO) scheme is used. The modified CO scheme operates just like the single point crossover defined in Eqs. (8) and (9) with the difference that l in Eq. (4) now runs from 1 to k (instead of $l = k$ to n), if the kth site has been chosen for crossover. The dramatic improvement in the convergence rate brought in by the new single point CO

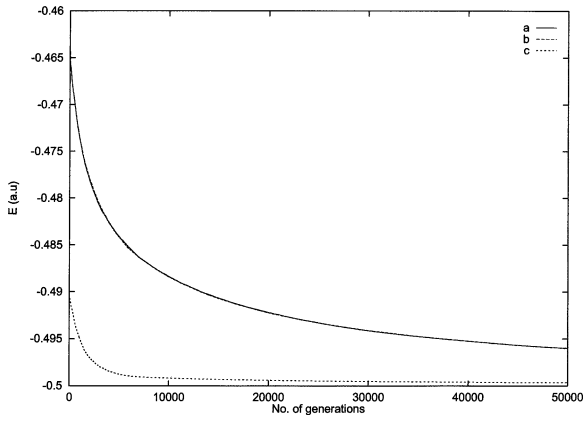


Fig. 3. The plot compares the computed energy evolution profile of the H-atom in the ground state for diffferent crossover schemes: (a) when simple single point arithmetic crossover scheme is used; (b) with multisite crossover; (c) with a modified single point crossover mentioned in Section 3.2 (mutation probability and intensity were held fixed in all the cases).

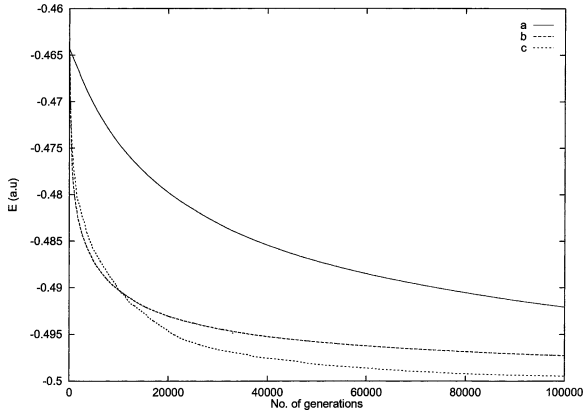
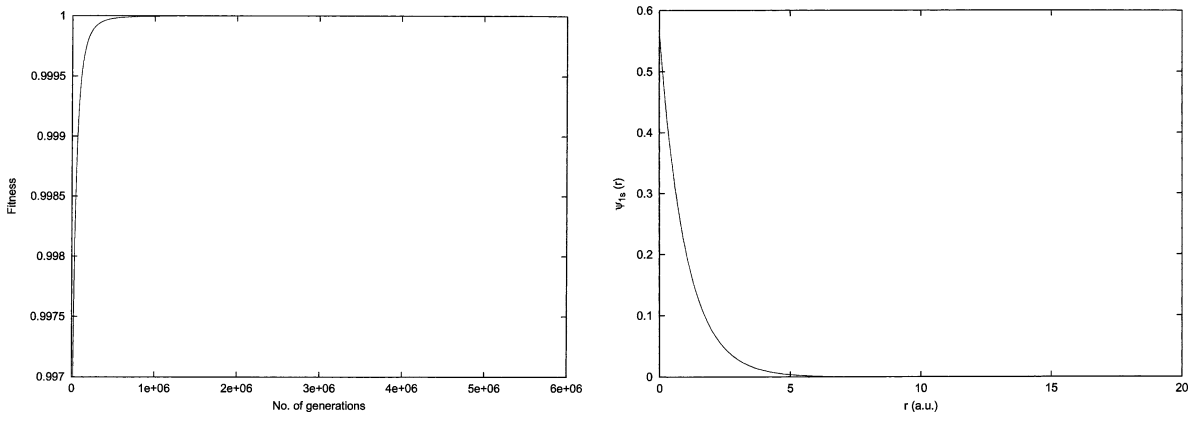


Fig. 4. The plot compares the computed energy evolution profile of the H-atom in the ground state with different models for adjusting mutation intensity in different generation: (a) constant mutation intensity was used throughout the evolution; (b) mutation intensity is an inversely changing function of the number of generations (cf. Eq. (11)); (c) mutation intensity is a continuously diminishing function of n_g, the specific form being chosen to be $\Delta(n_g, y) = y[1 - r^{(1-n_g/T)^l}]$ (see Eq. (12)).



(a) (b)

Fig. 5. (a) The fitness profile during the GA run for the H-atom in the ground state. The fitness corresponds to the string of the highest fitness in any generation. (b) The plot of GA optimized ground state wave function of the H-atom.

scheme has its origin in the fact that the space near the nucleus is the most important region in the H-atom contributing to the energy and the new scheme allows the algorithm to sample this region more frequently. The major improvements in the strings occur very rapidly under this new CO scheme. Thus, for Coulomb problems, the modified CO scheme is recommended.

Fig. 4(a) displays the energy evolution profile when the constant mutation intensity model is used throughout while Figs. 4(b) and (c) show the improvement as we switch over to schemes using dynamic adjustment of mutation intensity. In all the cases mutation probability (p_m) was held fixed at 0.05 and the single point CO scheme used. Clearly, the dynamic mutation intensity model (cf. Eq. (10)) leads to a very significant improvement in the convergence rate in the initial phase of the evolution.

The fitness profile for the best string in each generation is displayed in Fig. 5(a). It shows that the fine adjustments in the strings take place slowly during the latter stages of evolution. The string with the highest fitness in the converged population maps out the best representation of the genetically computed wave function which is displayed in Fig. 5(b). We have checked it against the known exact solution and found very good pointwise agreement (maximum difference in $|\psi|^2 \sim 10^{-8}$).

For the first excited state, the evolution of the fitness of the best string is shown in Fig. 6(a) while the corresponding energy evolution is presented in Fig. 6(b). We have also monitored the extent of satisfaction of the orthogonality constraint during the evolution (Fig. 6(c)). In these calculations we did not make all the strings in the population explicitly orthogonal to the exact ground state at every generation but used the *orthogonality condition as an explicit constraint in the objective function* (β *in* Eq. (13) *was set equal to* 1). The oscillations noticed in the plot of $\langle\phi|\psi\rangle$ is due to a rather expanded scale used here. The computed radial wave function for the $2s$ state is shown in Fig. 4(d) which agrees with the known Ψ_{2s} very well. We have a feeling that the presence of many constraints in the objective function can make optimization difficult when exploration of the search space is made by the GA. Alternative strategies of handling multiple constraints need to be explored in this connection.

3.3. Two-dimensional coupled harmonic oscillator problem

The system is described by the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\left\{\nabla_x^2 + \nabla_y^2\right\} + \frac{1}{2}\left(x^2 + y^2\right) + \lambda x^2 y^2 \quad (\lambda = 0.1). \tag{16}$$

The wave function $\Psi(x, y)$ is represented via an amplitude distribution on a 2-d grid (120×120 points).

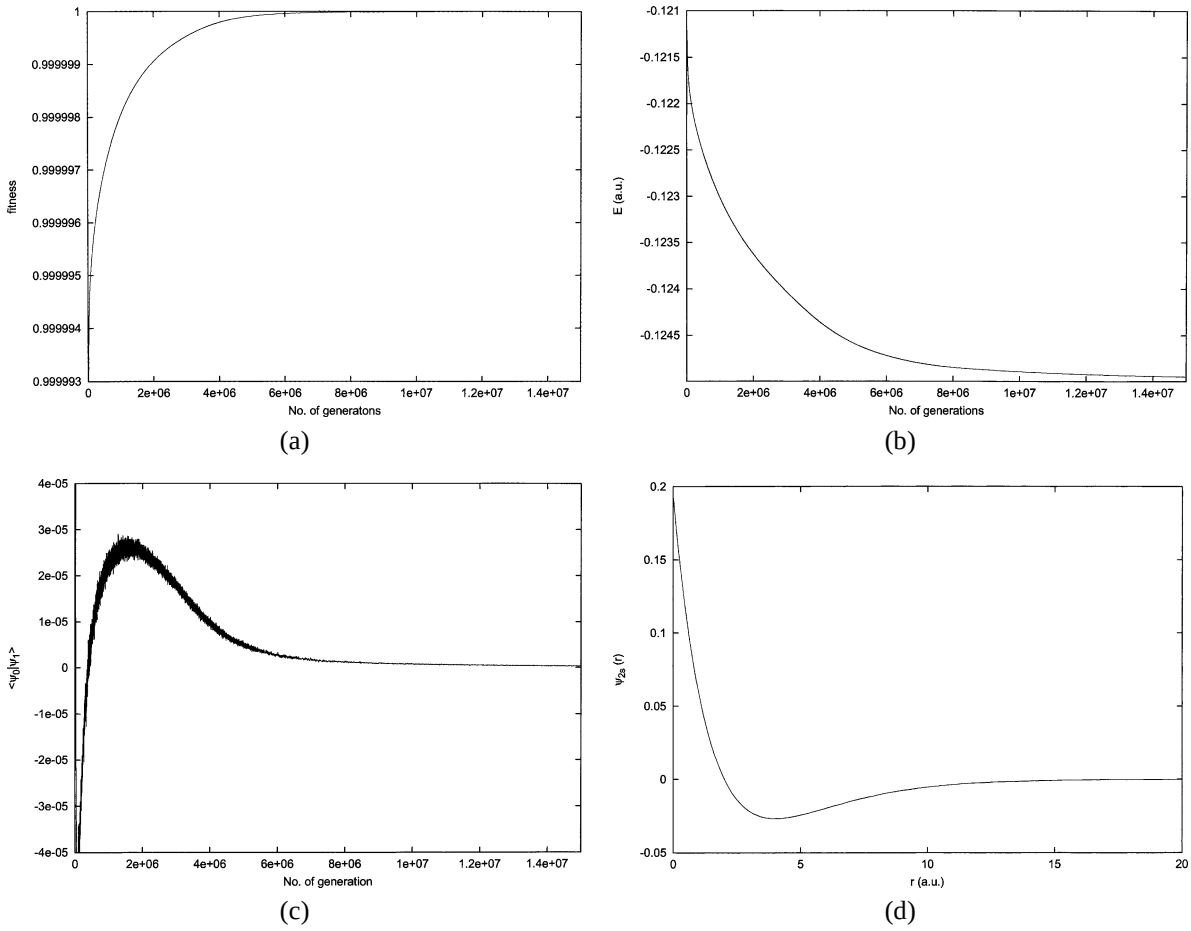
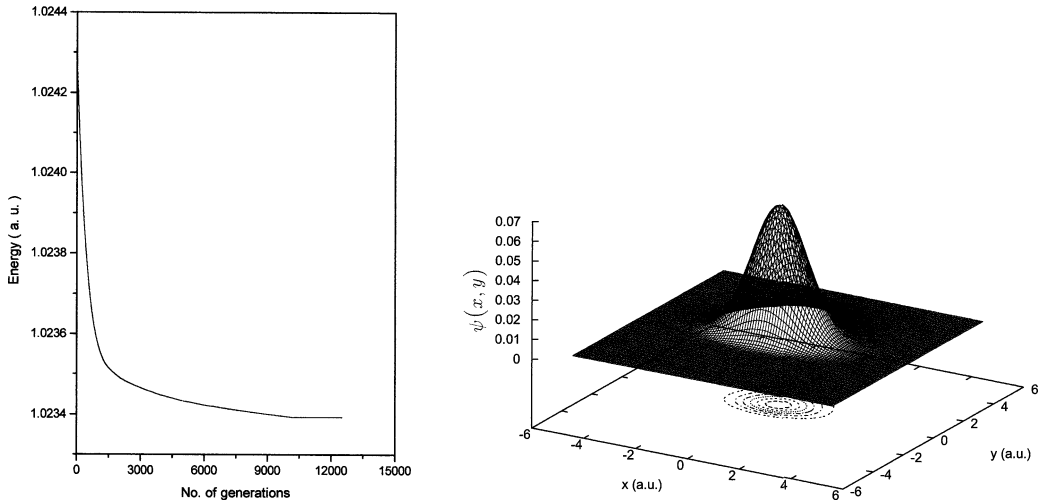


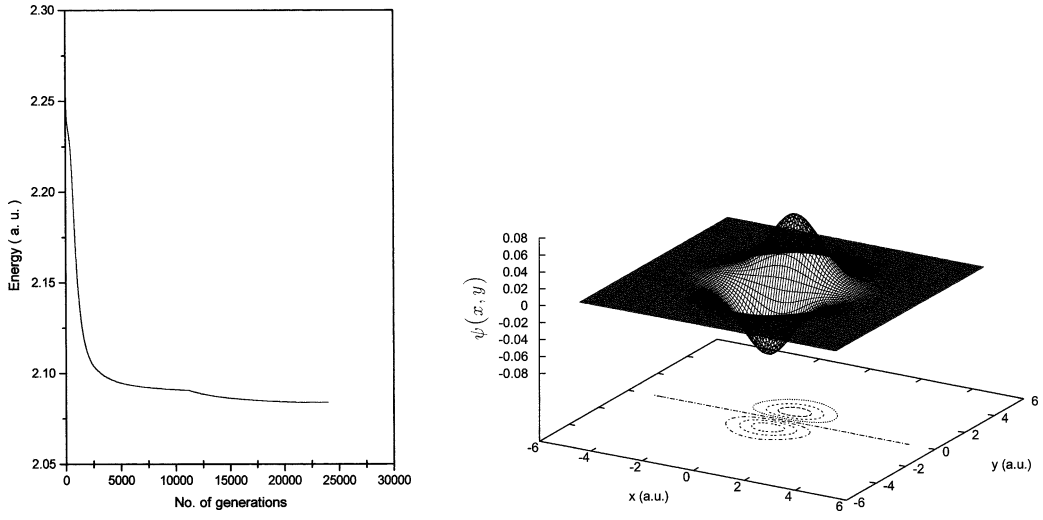
Fig. 6. (a) The fitness profile during the GA run for the H-atom in the first excited state. (b) Evolution of energy for the first excited state of the H-atom during the GA run. (c) Evolution of orthogonality integral during the GA run for the first excited state of the H-atom. (d) The plot of GA optimized first excited state wave function of the H-atom.

Each string in this case is a collection of 14400 amplitudes and 10 such strings made up the population. For quadrature, additional points were generated by a two-dimensional bicubic interpolation. The energy profile obtained by following the energy of the best string in the population at each generation is shown in Fig. 7(a) while the 3-d plot of the wave function obtained from the amplitudes making up the best string in the converged population is displayed in Fig. 7(b). The converged energy (1.023383) and the wave functions compare well with those obtained from the FGH calculation (1.023393 a.u.). For the first excited state, the energy profile behaves similarly (Fig. 8(a)). While the final wave function displayed in Fig. 8(b) compare well with the FGH counterpart, the energy (2.0839558 a.u.) also turns out to be quiet accurate. The two-dimensional oscillator problem gives us an indication as to how one could possibly handle a two electron problem by GA. The two (interacting) electron radial SE can, in fact be handled similarly while solution of the full problem would require explicit handling of much more complex strings describing the amplitude distribution in a six-dimensional coordinate space. The ground and excited states of two electron atoms pose no particular problem regarding enforcement of anti symmetry requirements of the many Fermion wave functions as the space and spin parts are separable. Beyond two electrons, one needs to use projection opera-



(a) (b)

Fig. 7. (a) Evolution of energy for the ground state of the 2-d anharmonic oscillator (the anharmonic term is $\lambda x^2 y^2$ with $\lambda = 0.1$) during the GA run. (b) The 3-d plot (including the contour) of the GA optimized wave function for the ground state of 2-d anharmonic oscillator.



(a) (b)

Fig. 8. (a) Evolution of energy for the first excited state of the 2-d anharmonic oscillator referred in Fig. 7(a). (b) The 3-d plot (including the contour) of the GA optimized wave function for the first excited state of the 2-d anharmonic oscillator referred in Fig. 7(a).

tors to impose antisymmetry on the probability amplitude distribution computed directly. We will address these problems in a separate communication [16]. We may note, however, that similar problems have been handled in quantum Monte Carlo approach [15].

The results presented here raise hope that the GA based recipes may prove to be a viable alternative for calculating the wave functions and energies of the stationary states of low-dimensional systems. We feel that the basic scheme may well be extended to systems

of larger dimensions for which a few additional features have to be incorporated in the algorithm:

(1) The algorithm has to be parallelized. Particularly, evaluation of different strings should be done parallely. The crossover of each pair and the mutation of different strings can also be parallelized, saving a lot of computer time. In the scalar mode, the algorithm works rather slowly towards the end of the search.
(2) For higher-dimensional problems, the Monte Carlo integration should replace quadratures used here.
(3) One should use the accumulated information over a number of generations to project the population at a future generation by using suitable extrapolation techniques and achieve faster convergence.
(4) More accurate quadratures, if used, can cut down number of grid points to be used explicitly.
(5) The initial population may be generated by exploiting the information about approximate wave functions of the systems under consideration. We have avoided doing that in the present studies as we wanted to test the performance of the algorithm in the most demanding situation.

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