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# Numerical solutions of the Schrödinger equation directly or perturbatively by a genetic algorithm: test cases

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**Abstract**

The workability of a genetic algorithm-based strategy to solve the Schrödinger equation directly is tested with reference to a screened Coulomb potential and an oscillator with quartic anharmonicity. The suitability of the same basic idea in solving the inhomogeneous differential equations of Rayleigh–Schrödinger perturbation theory is also examined in this context with particular reference to the ground state of a two-electron atom. Special advantages of the general approach are stressed. 

## 1. Introduction

Very few quantum mechanical problems can be solved exactly and analytically. A numerical solution of the Schrödinger equation may be a feasible alternative. Otherwise, one is compelled to look for approximate methods of one kind or another for arriving at meaningful solutions. For a class of problems, Rayleigh–Schrödinger perturbation theory (RSPT) [1] works well and is frequently used. The inhomogeneous differential equations that RSPT leads to are seldom solved directly to determine the corrections ($\psi_n^{(1)}$, $\psi_n^{(2)}$, etc.) to the unperturbed function at different orders. Instead, one expands the correction functions in the complete ortho-normal set provided by the solutions of the unperturbed energy eigenvalue equation and obtains the familiar sum-over-states expressions for the perturbed wavefunctions and perturbed energy eigenvalues. However, if $\psi_n^{(1)}$, $\psi_n^{(2)}$, etc., could be found analytically or even numerically just like the unperturbed function $\psi_n^{(0)}$, one could avoid the sum-over-states route and obtain the energy at different orders directly. The *F*-function technique which was developed and successfully used by Dalgarno and Lewis [2,3] is an example of what can be achieved by going for direct solution of the inhomogeneous differential equations of RSPT. Few examples are, however, available in the literature [1–4] where one has actually bypassed the sum-over-states prescripion in favour of a more direct and sometimes closed-form solution of the problem.

In the present Letter, we propose to explore direct routes that attempt to solve the relevant Schrödinger equations or their perturbative counterparts numerically. The energy eigenvalue equation (the Schrödinger equation), for example, is sought to be solved directly, providing $\psi_n$ and $E_n$. It requires us to solve a homogenous differential equation by a numerical recipe. In the perturbative approximation (RSPT), we

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solve the set of inhomogeneous differential equations for the problem concerned by adopting essentially the same numerical recipe adopted in solving the eigenvalue problem. The numerical method of our choice is a non-deterministic, derivative-free optimizer called the genetic algorithm (GA) [5–7]. For invoking GA, we cast the problem in each case as an appropriate maximization problem of an abstract fitness function on a rather rugged fitness landscape (see later). The implementation of GA realized in the present work uses floating-point representation of the solution strings instead of binary representation which appears to be more common in a GA-based search for optima.

## 2. Genetic algorithm and solution of the Schrödinger equation

We consider two different approaches for solving the energy eigenvalue problem.

### 2.1. Direct solution by genetic algorithm

The solution of the Schrödinger equation for the stationary states of a system involves solution of the homogeneous differential equation under appropriate boundary conditions:

$$(H - E_n) \mid \psi_n\rangle = 0\,. \tag{1}$$

Numerically, the problem boils down to finding a suitable function $\psi_n$ and a corresponding scalar $E_n$ such that the norm of the vector $\boldsymbol{\zeta}_n = (H - E_n) \mid \psi_n\rangle$ is zero. Our contention is that GA [5–7] can provide an efficient search algorithm for finding $\psi_n$ and $E_n$ in one go.

### 2.2. Perturbative solution by genetic algorithm

Let the Hamiltonian be partitioned into $H_0$ (unperturbed Hamiltonian) and a perturbation $\lambda V$, $H = H_0 + \lambda V$. Application of RSPT with intermediate normalisation then leads to the following inhomogeneous differential equations for $\psi_n^{(1)}$, $\psi_n^{(2)}$, etc.

$$\left(H_0 - E_n^{(0)}\right)\psi_n^{(1)} = \left(E_n^{(1)} - V\right)\psi_n^{(0)}\,, \tag{2}$$

$$\left(H_0 - E_n^{(0)}\right)\psi_n^{(2)} = \left(E_n^{(1)} - V\right)\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}\,, \tag{3}$$

where $\left(H_0 - E_n^{(0)}\right) \mid \psi_n^0\rangle = 0$. $\psi_n^{(1)}$, $\psi_n^{(2)}$, $E_n^{(1)}$, $E_n^{(2)}$, etc., are corrections to the perturbed wavefunctions and energies at different orders.

Since $E_n^{(1)}$ in Eq. (2) is equal to $\langle \psi_n^{(0)} \mid V \mid \psi_n^{(0)}\rangle$, and $E_n^{(0)}$ and $\psi_n^{(0)}$ are known to start with, one can hopefully solve it directly for $\psi_n^{(1)}$. Once $\psi_n^{(1)}$ is known it can be used to obtain $E_n^{(2)} = \langle \psi_n^{(0)} \mid V \mid \psi_n^{(1)}\rangle$. Using the known value of $E_n^{(2)}$ and the function $\psi_n^{(1)}$ now in Eq. (3) one can solve the equation for $\psi_n^{(2)}$ directly by GA [5–7]. Having defined the problem of our immediate interest, we now introduce the genetic algorithm as the specific tool for solving Eqs. (1)–(3).

### 2.3. Genetic algorithm

Optimization problems are of varied types and complexities. There are problems which require large-scale combinatorial optimization and there are those which involve highly constrained optimization. Genetic algorithms aim at solving such complex problems. The most important property of these algorithms is that they work on a population of potential solutions while all other methods process a single point in the search space. The population of potential solutions is allowed to undergo a simulated evolution in the sense that at each generation the relatively good solutions are allowed to stay on and reproduce while the bad ones are allowed to die out. To discriminate between different solutions one makes use of an objective function which plays the role of the environment. New solutions are generated from the old ones by simulated genetic operations of crossover and mutation. Traditionally, GAs are implemented on binary strings. The nature of the problem at hand demands that we use a coding that allows the GA to operate as closely as possible in the space of the original problem. We have, therefore, implemented GA on floating-point strings. The basic idea employed in this implementation is illustrated with reference to Eq. (1).

#### 2.3.1. Solution of the energy eigenvalue equation

Let the range $R$ of integration of Eq. (1) for $\psi_n$ be from 0 to $a$. $R$ is divided into a grid of $M$ points (*not necessarily equispaced*). A probable solution $\psi_{n_i}$ is then modelled by a string of floating-point numbers collected into a vector $\boldsymbol{s}_i \equiv (g_1^i, g_2^i,$

$\ldots, g_M^i)^t \equiv \psi_{n_i}$ (say). $g_m^i$ represents the value of the function $\psi_{n_i}$ at the $m$th point ($r_m$) in space. $\psi_{n_i}$ is appropriately normalised and the corresponding energy ($E_{n_i}$) is set equal to $\langle \psi_{n_i} | H | \psi_{n_i} \rangle / \langle \psi_{n_i} | \psi_{n_i} \rangle$. A set of $N_p$ such feasible or trial solutions are chosen to start with. $N_p$ is thus the size of the population that is to be genetically processed. These feasible or trial solutions will not satisfy Eq. (1) and the magnitude of the error can be estimated by computing the quantity ($\sigma_i$) where

$$\theta_i = \left(H - E_{n_i}\right)\psi_{n_i}, \quad \sigma_i = \left\{|\theta_i|^2\right\}^{1/2}. \tag{4}$$

The fitness of the $i$th feasible solution having residue $\theta_i$ is defined to be

$$f_i = \mathrm{e}^{-\sigma_i}. \tag{5}$$

The maximum fitness in this representation is 1 and is achieved only when $\psi_{n_i}$ satisfies Eq. (1) at each of the $M$ points in the discretized space of integration. All other trial solutions are characterized by $0 < f_i < 1$. Once each member of the initial population of strings has been evaluated for their fitness, the standard roulette-wheel selection procedure [5] is used for preparing a population of size $N_p$ in which the strings with above-average fitness have more copies. The binary genetic operator (crossover) is then applied to randomly selected pairs of solution strings ($s_m, s_n$) with a predefined crossover probability $p_c$ ($\sim 0.25$). For the floating-point strings used, a uniform crossover mechanism has been adopted. The two new strings produced by uniform crossover are

$$\left.\begin{aligned} s'_m &= p_1 s_m + p_2 s_n \\ s'_n &= p_2 s_m + p_1 s_n \end{aligned}\right\} \tag{6}$$

where $p_2 = 1 - p_1$, and $p_1$ is randomly chosen from the interval $a_c \leqslant p_1 \leqslant b_c$.

After the strings are all exhausted for crossover operation, the new population of $N_p$ strings ($s'_1, \ldots, s'_m$) is allowed to undergo the unary genetic operation of mutation with probability $p_m$ (0.01–0.1). The operation is simple to carry out on a floating-point string. Let us suppose that the $l$th grid-point value of the $m$th string has been chosen for mutation. Then the string

$$s'_m = (g'_1, g'_2, \ldots, g'_l, \ldots, g'_n) \tag{7}$$

is replaced by

$$s''_m = (g'_1, g'_2, \ldots, g''_l, \ldots, g'_n) \tag{8}$$

where

$$g''_l = g'_l + (-1)^L r s. \tag{9}$$

In Eq. (9) $L$ is a random integer, $r$ is a random number with $0 \leqslant r \leqslant 1$ and $s$ has a small value ($\sim 10^{-3} \leqslant s \leqslant 10^{-2}$). After each member of the population of $N_p$ strings has been subjected to mutation, they are normalised and the genetically altered members of the population are used to compute the corresponding $E'_{n_i}\left[ = \langle \psi'_{n_i} | H | \psi'_{n_i} \rangle \right]$ and the fitness of each processed string is computed. These new strings together with an equal number of old strings belonging to the previous generation are passed on for selection in the roulette-wheel procedure. After a number of such cycles have been repeated, usually the average fitness $f_{\mathrm{av}}$ and the maximum fitness of the population tend to become equal to 1 ($f_{\mathrm{av}} = f_{\max} \rightarrow 1$). The string of maximum fitness is then hopefully the solution function we have been looking for and the corresponding $E_n$ (best) is the desired eigenvalue.

### 2.3.2. Solution of perturbative equations for energy

Let us now turn to the perturbative calculation of energy. The inhomogeneous differential Eqs. (2) and (3) and similar equations for still higher orders are of the general type

$$\left(H_0 - E_n^0\right)\psi_n^{(m)} = \chi_n. \tag{10}$$

These equations are seldom analytically solvable. The numerical integration of these equations may often pose problems as they are to be solved under the constraint $\langle \phi_n^{(0)} | \phi_n^{(m)} \rangle = 0$. One case where one can write down an expression for $\psi_n^{(m)}$ in closed form and even evaluate it by quadrature [8] is a one-dimensional problem with $H_0 = (-\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}x^2) + V(x)$,

$$\psi_n^{(m)}(x) = \frac{2m}{\hbar^2}\phi_n^0 \int_0^x \frac{1}{\phi_n^{02}}\,\mathrm{d}x' \times \int_{-\infty}^{x'} \chi(x'')\,\phi_n^0(x'')\,\mathrm{d}x''. \tag{11}$$

One must be careful to note the zeros of $\phi_n^0$ while using Eq. (11). However, the approach outlined for solving the eigenvalue equations can be equally viable for solving the inhomogeneous differential Eqs. (2) and (3). The only departure from the homoge-

neous case occurs in the definition of $\sigma_i$ which now reads

$$\sigma_i = \left[ \left| \left\{ \left( H_0 - E_n^0 \right) \psi_n^{(m)} \right\} - \chi_n \right|^2 \right]^{1/2}$$

and in the fact that the expectation value of $H$ no longer needs to be computed while solving equations of type (10), in general.

## 3. Model problems

We propose to test the algorithm suggested in Section 2 for finding energy eigenvalues of the well-known [9–12] screened Coulomb (SC) and the quartic anharmonic oscillator (AO) problems either directly or perturbatively.

### 3.1. Energy eigenvalues of the screened H-atom

The radial Schrödinger equation for this problem is

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}r^2\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1)}{r^2}\right)R(r) - \left(\frac{Ze^2}{r}e^{-r/D}\right)R(r) = E_{nl}R(r)\,. \tag{12}$$

A numerical solution of this equation in $r$-space would encounter difficulties for a given $n$ and $l$ as solutions may not exist for a screening length $D < D^{n,l}_{\text{critical}}$, the latter being an unknown positive number that depends upon $Z,n,l$. The difficulty can be avoided by making the following transformation [12]:

$$\left.\begin{aligned} \rho &= \left(\frac{2z}{a_0}\right) r\lambda_{n,l}^{-1} \\ \sigma_d &= \left(\frac{2z}{a_0}\right) D\lambda_{n,l}^{-1} \\ E_{n,l} &= \frac{z^2\hbar^2}{2a_0^2 m}\lambda_{n,l}^{-2} \end{aligned}\right\} \tag{13}$$

where $\lambda_{n,l}$s are the eigenvalues of the radial SE in the $\rho$ space and $d$ is the transformed screening length. The transformation enables one to compute the solution of the RSE for $0 \leqslant d \leqslant \infty$. The transformed RSE reads

$$\frac{\mathrm{d}^2R}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}R}{\mathrm{d}\rho} + \left(\frac{\lambda_{nl}e^{-\rho/d}}{\rho} - \tfrac{1}{4} - \frac{l(l+1)}{\rho^2}\right)R = 0 \tag{14}$$

and can be solved directly by GA. The solution of the AO problem can proceed similarly. The relevant equation to be solved is

$$\frac{-\hbar^2}{2m}\frac{\mathrm{d}^2\psi_\nu}{\mathrm{d}x^2} + \left(\frac{kx^2}{2} + \lambda x^4 - E_\nu\right)\psi_\nu = 0\,. \tag{15}$$

We have solved Eq. (15) for $\lambda = 0.1$, 0.2 and 0.3 by GA and compared with accurate variational results.

### 3.2. Perturbative solution of the screened Coulomb problem

The perturbative solution of the SC problem requires a suitable zeroth order Hamiltonian ($H_0$). A simple way of choosing $H_0$ can be as follows. The Hamiltonian of a particle moving in a SC potential $V(r) = -\alpha e^{-\lambda r}/r$ is given by

$$H = -\frac{1}{2m}\nabla_r^2 - \alpha\frac{e^{-\lambda r}}{r} \tag{16}$$

where

$$\nabla_r^2 = \frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\,.$$

We can construct a repartitioned Hamiltonian as follows:

$$H = -\frac{1}{2m}\nabla_r^2 - \frac{\beta}{r} + \left(\frac{\beta}{r} - \alpha\frac{e^{-\lambda r}}{r}\right) = H_0 + \beta\left(\frac{1}{r} - \frac{\alpha e^{-\lambda r}}{\beta r}\right) = H_0 + \beta V\,. \tag{17}$$

The unperturbed Hamiltonian of Eq. (17) represents an unscreened hydrogenic atom (nuclear charge $= \beta$) with known energy eigenfunctions and eigenvalues.

The RSPT equations for the repartitioned problem are:

$$\left(-\frac{1}{2m}\nabla_r^2-\frac{\beta}{r}\right)\psi_n^{(0)}=E_n^{(0)}\psi_n^{(0)}\,, \tag{18}$$

$$\left\{\left(-\frac{1}{2m}\nabla_r^2-\frac{\beta}{r}\right)-E_n^{(0)}\right\}\psi_n^{(1)} = \left\{\langle\psi_n^{(0)}\mid\frac{1}{r}-\frac{\alpha e^{-\lambda r}}{\beta r}\mid\psi_n^{(0)}\rangle - \left(\frac{1}{r}-\frac{\alpha e^{-\lambda r}}{\beta r}\right)\right\}\psi_n^{(0)}\,, \tag{19}$$

$$\left\{\left(-\frac{1}{2m}\nabla_r^2-\frac{\beta}{r}\right)-E_n^{(0)}\right\}\psi_n^{(2)} = \left\{\langle\psi_n^{(0)}\mid\frac{1}{r}-\frac{\alpha e^{-\lambda r}}{\beta r}\mid\psi_n^{(0)}\rangle - \left(\frac{1}{r}-\frac{\alpha e^{-\lambda r}}{\beta r}\right)\right\}\psi_n^{(1)}+\langle\psi_n^{(1)}\mid\frac{1}{r} -\frac{\alpha e^{-\lambda r}}{\beta r}\mid\psi_n^{(0)}\rangle\psi_n^{(0)}\,. \tag{20}$$

Eqs. (18) and (20) can only be solved one after another as each succeeding equation requires the information obtained from the preceeding one for solution. The derivatives are calculated numerically. Once $\psi_n^{(0)}$, $\psi_n^{(1)}$ and $\psi_n^{(2)}$ are obtained, the energy $E_n''(\lambda)$ can be obtained from the functional

$$E_n''(\lambda)=\frac{\langle\psi_n^{(0)}+\beta\psi_n^{(1)}+\beta^2\psi_n^{(2)}\mid H\mid\psi_n^{(0)}+\beta\psi_n^{(1)}+\beta^2\psi_n^{(2)}\rangle}{\langle\psi_n^{(0)}+\beta\psi_n^{(1)}+\beta^2\psi_n^{(2)}\mid\psi_n^{(0)}+\beta\psi_n^{(1)}+\beta^2\psi_n^{(2)}\rangle}\,. \tag{21}$$

A lower-order estimate of the energy $E_n'(\lambda)$ is given by a similar expression in which terms containing $\beta^2$ are dropped.

$$E_n'(\lambda)=\frac{\langle\psi_n^{(0)}+\beta\psi_n^{(1)}\mid H\mid\psi_n^{(0)}+\beta\psi_n^{(1)}\rangle}{\langle\psi_n^{(0)}+\beta\psi_n^{(1)}\mid\psi_n^{(0)}+\beta\psi_n^{(1)}\rangle}\,. \tag{22}$$

$E_n'(\lambda)$ and $E_n''(\lambda)$ provide upper bounds to the energy of the SC system. Similar equations can be worked out for other problems once the Hamiltonian is partitioned into $H_0$ and the perturbation, $\lambda V$. We will discuss in particular the quartic AO problem ($H=(p_x^2/2m)+1/2kx^2+\lambda x^4$, $k=1.0$ and $\lambda=0.1$) as a second example.

## 4. Results and discussion

### *4.1. Direct solution of the screened Coulomb and anharmonic oscillator energy eigenvalue problem*

For the SC problem, we solve Eq. (14) directly for the ground state. The $\rho$ space is discretized $\{\rho_i\}_{i=1,n}$ and $m$ strings $\{R_{mi}\}$ are generated. $\{R_{mi}\}$ stands for the value of the $m$th wavefunction at the $i$th point in $\rho$ space. For each string $\{R_m(\rho_i)\}\equiv\{R_{mi}\}$, $i=1,n$. $\mathrm{d}R/\mathrm{d}\rho$ and $\mathrm{d}^2R/\mathrm{d}\rho^2$ are calculated by a finite difference method and the magnitude of the expression on the LHS of Eq. (14) is evaluated from which the fitness of the given string is calculated as described in Section 2. We have used a population of 100 and a grid of 100 points covering a length of 10 a.u. The profile of the fitness of the best individual is shown as a function of generation along with the evolution of $\lambda_{1,0}$, for the ground state when $D=0.06$ (Fig. 1a,b). The fitness profile converges quite fast to make the method attractive. From the converged values, $\lambda_{1,0}$ turns out to be equal to 1.10937 a.u. which means that the energy eigenvalue for the ground state is $-0.40627$ a.u. This agrees with available results on the system concerned [9–12]. There are certain advantages in adopting the GA-based approach. For example, we could have transformed Eq. (14) to a finite difference equation and integrated it for $R(\rho)$ [12]. But, for calculating $\lambda_{n,l}$ we would have required to compute the sign changes of $R(\rho)_{\rho\to\infty}$ by successively increasing the trial $\lambda_{nl}$ values ($\lambda_0$) by $\Delta\lambda$, $2\Delta\lambda$, …, $n\Delta\lambda$, for bracketing the eigenvalues within a range $\Delta\lambda$. This step is redundant in our approach *as the computation of* $\lambda$ *takes place simultaneously with that of* $R(\rho)$. So, once the string with the best fitness has been identified, the corresponding energy eigenvalue becomes simultaneously known. The method is robust also, for if the $\lambda_{nl}$ values for different strings are perturbed away from their current values forcibly,

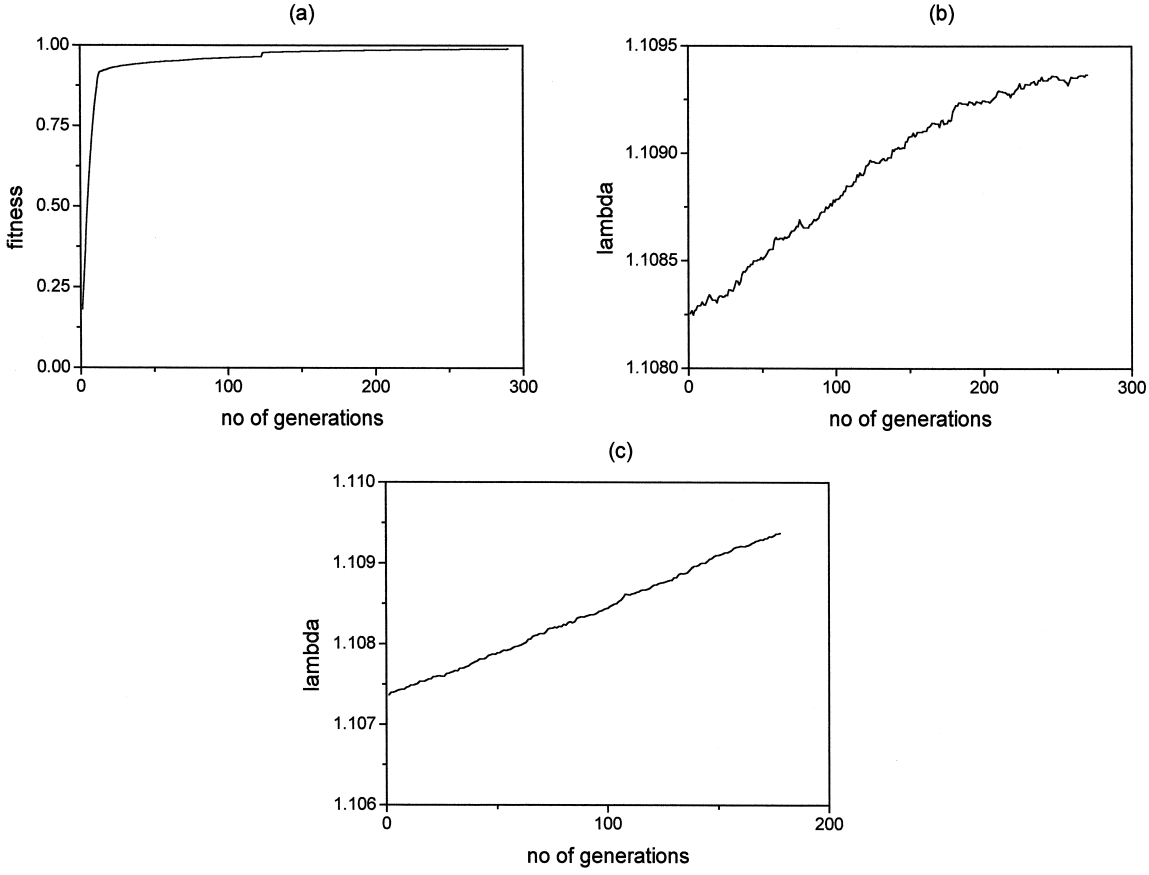


Fig. 1. (a) Evolution of the fitness function shown against number of generations elapsed during the direct solution for the ground-state energy of the screened H-atom. (b) Evolution of eigenvalue $\lambda_{1,0}$ observed during GA-based direct solution of the Schrödinger equation for the ground state of screened H-atom problem. (c) Evolution of $\lambda_{1,0}$ against the number of generations after being perturbed arbitrarily away from the correct value. It shows the robustness of the algorithm.

they quickly correct themselves during the evolution (Fig. 1c).

The solution for the ground state of the 1-d quartic AO ($\lambda = 0.1,\ 0.2,\ 0.3$) proceeds similarly. We have used a polulation size of 100, 150 grid points and a grid of length 15 a.u. The energy of the string of the highest fitness ($\lambda = 0.1$) turns out to be 0.559147 a.u. while the ground-state energy predicted by the Fourier Grid Hamiltonian [14,15] method with 151 grid points and a grid length of 15 a.u. is found to be 0.559146 a.u. Table 1 presents energy values obtained with a population size of 100, 150 grid points and a grid length of 15 a.u. They compare well with variational results.

### *4.2. Perturbative results for the screened Coulomb and anharmonic oscillator problem*

We first consider a perturbative solution of the SC problem. Eqs. (19) and (20) have been solved by GA

Table 1
Eigenvalues for the quartic oscillator problem at various λs. Variational results (FGH) are included for comparision

| λ | GA result | Variational result |
|---|---|---|
| 0.1 | 0.559147 | 0.559146 |
| 0.2 | 0.602405 | 0.602405 |
| 0.3 | 0.6379925 | 0.637992 |

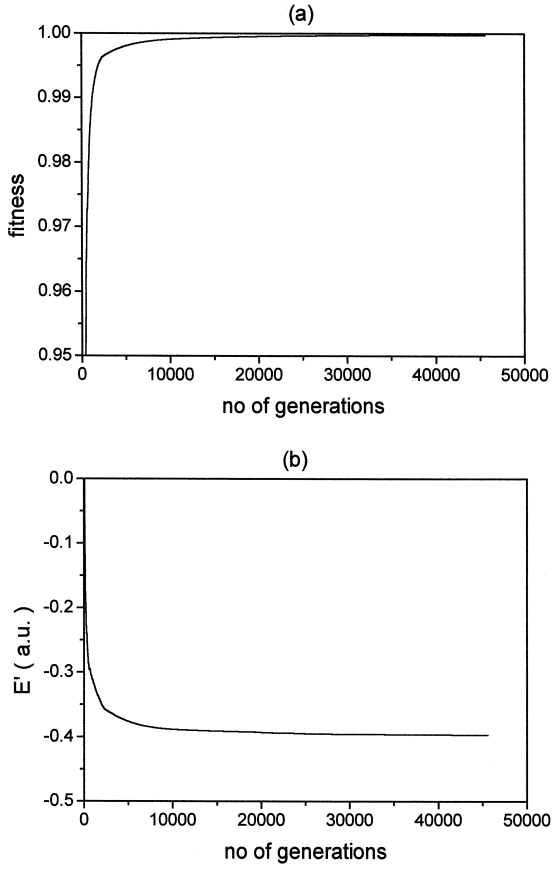


Fig. 2. (a) The fitness profile observed during the solution of the first-order correction ($\psi_0^{(1)}$) to the ground-state wavefunction in the SC problem. (b) The energy ($E_0'(\lambda)$, (cf. Eq. (22)) plotted against the number of generations during the genetic evolution of the first-order correction ($\psi_0^{(1)}$) to the ground-state wavefunction.

for $\alpha = 1.0$, $\lambda = 0.1$, as a test case. Other values of $\alpha$ and $\lambda$ can be used with equal facility if $\lambda < \lambda_c$. Fig. 2a,b display how the fitness of the best string in each generation (Fig. 2a) evolves and the corresponding ground-state energy $E_0'$ (Fig. 2b) while solving Eq. (19), for example, for the ground state of the SC potential with $\lambda = 0.1$. The best string in this case represents the closest approximation to the function $\psi_0^{(1)}$. As the system with a population size of 100 strings is allowed to evolve genetically (each string has 100 amplitudes for $\psi_0^{(1)}$ at 100 different points in space) the fitness of the best individual in the population begins to increase quickly and asymptotically approaches the limiting value of $f_{\max} = 1$, as the number of generations $n_g \to \infty$. The energy $E_0'$ computed with the best string shows a gradual decrease and eventually reaches a limiting value. Fig. 3a displays the fitness evolution profile for $\psi_0^{(2)}$. The pattern of evolution looks much the same as observed for $\psi_0^{(1)}$. The energy computed with the best string representing $\psi_0^{(2)}$, i.e. $[E_0''(\beta,\lambda)]$ at each generation ($n_g$) is plotted in Fig. 3b. The energy profile appears to be just the inverse of the fitness profile. The energy is high when the fitness is low, and low when the fitness is high. $[E_0''(\beta,\lambda)]$ shows saturation as the evolution is continued through a large number of generations ($n_g \to \infty$). The parameter $\beta$ appearing

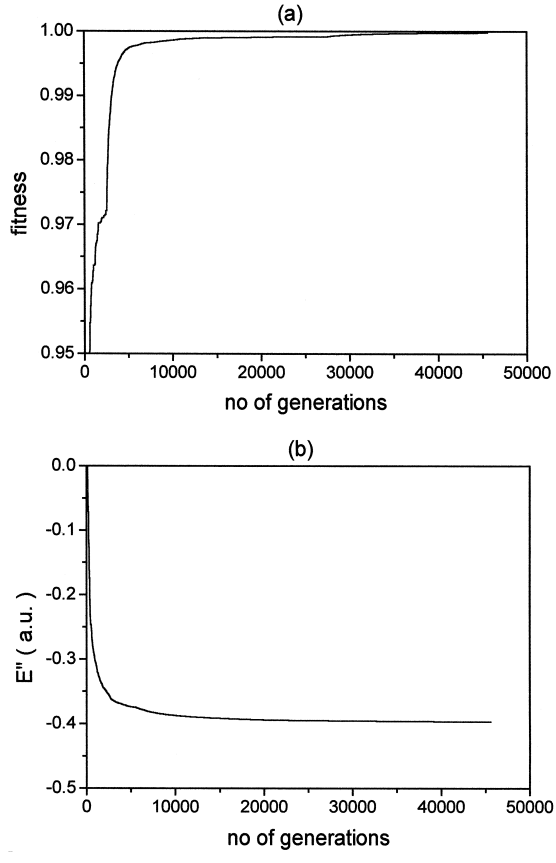


Fig. 3. (a) The fitness profile observed during the genetic evolution of the second-order correction ($\psi_0^{(2)}$) to the ground-state wavefunction in the SC problem. (b) The energy ($E_0''(\lambda)$ (cf. Eq. (21)) shown against the number of generations elapsed during the calculation of the second-order correction ($\psi_0^{(2)}$) to the ground-state wavefunction in the SC problem.

Table 2
Ground-state energies (in a.u.) in the SC problem approximately correct to third ($E'$) and fifth order ($E''$) for various $\beta$s at fixed $\alpha$ and $\lambda$. Variational (these correspond to small non-orthogonal CI calculations in a spherical oscillator basis with $l=0$) results are included for comparision

| $\alpha$ | $\beta$ | $\lambda$ | $E'(\lambda)$ | $E''(\lambda)$ | Variational result |
|---|---|---|---|---|---|
| 1.0 | 0.90 | 0.1 | −0.38684817 | −0.37232301 | |
| 1.0 | 0.95 | 0.1 | −0.39676029 | −0.38066466 | |
| 1.0 | 0.975 | 0.1 | −0.40269260 | −0.39662093 | −0.404843 |
| 1.0 | 1.0 | 0.1 | −0.39711789 | −0.38684817 | |
| 1.0 | 1.05 | 0.1 | −0.37556954 | −0.37924446 | |
| 1.0 | 1.1 | 0.1 | −0.37470734 | −0.35746940 | |
| 1.0 | 0.95 | 0.6 | −0.093220 | −0.0823418 | −0.103375 |

in the repartitioned Hamiltonian of Eq. (17) may appear to be arbitrary. Although infinite-order perturbation results would be independent of the particular value of $\beta$ used in defining $H_0$, results at finite orders could depend on it and more so at lower orders. This $\beta$ dependence of the energy at low orders can be exploited to choose an optimum $\beta$ that can lead to better convergence of the perturbation expansion [13]. In the present case $E_0(\beta,\lambda)$ computed with the perturbed wavefunction correct to second order in perturbation strength ($\beta$) (cf. Eq. (19)) when plotted against $\beta$ shows a clear minimum at $\beta=0.975$ when $\lambda=0.1$. We can hope that this particular choice of $\beta$ would define an optimal $H_0$ for RSPT calculation.

Table 2 reports the energy values computed at different orders (approximately third and fifth orders, respectively) of perturbation theory computed with $\beta_{\text{opt}}$ ($\lambda=0.1$) and $\beta_{\text{arbitrary}}$ ($\lambda=0.1$). Results obtained from a variational calculation are also included for comparision. It seems that $\beta_{\text{opt}}$ leads to faster convergence of the perturbed energy. It is to be noted that $\beta_{\text{opt}}$ depends on $\lambda$. As a further example, the result for $\lambda=0.6$ is included for comparision. $\beta_{\text{opt}}$ is significantly lower for the $\lambda=0.6$ case. However a number of calculations similar to those reported here can determine $\beta_{\text{opt}}(\lambda)$ once for all for the SC problem. The procedures followed remain applicable to the excited states for which $l\neq 0$ as well. The radial Hamiltonian in these cases will contain an additional term $l(l+1)/r^2$. We turn now to the 1-d quartic ($\lambda x^4$) AO problem ($H=(p_x^2/2m)+1/2kx^2+\lambda x^4$). The differential equation for $\psi_n^{(1)}$ is not amenable to solution in this case by the F-function method [2,3]. A direct solution by numerical integration of the Schrödinger equation is also difficult in this case. The sum-over-states expression for perturbation energies or wavefunctions involve finite sums in this case which allows us to compare the GA results with those of standard RSPT. Fig. 4a shows the fitness as a function of the number of generations as $\psi_0^{(1)}$ is optimized (for $\lambda=0.1$). Fig. 4b displays the plot of $\psi_0^{(0)}$ and $\psi_0^{(1)}$, the latter corresponding to the best string in the hundredth generation. The energy $E_n'(\lambda)$ corresponding to the calculated $\psi_0^{(1)}$ is 0.5581 a.u. which is in agreement

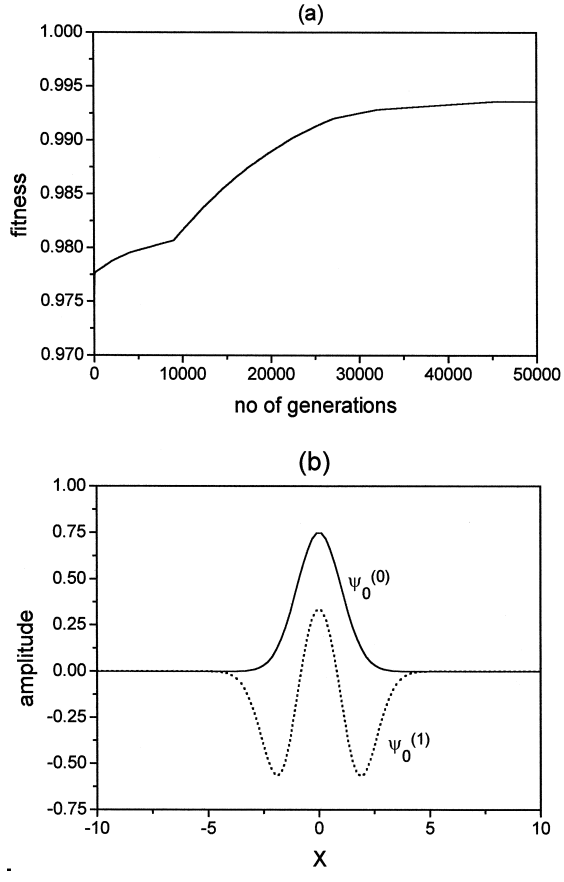


Fig. 4. (a) The fitness profile obtained during the solution of the first-order correction ($\psi_0^{(1)}$) to the ground-state wavefunction in the quartic AO problem. (b) The plots of the unperturbed ground-state wavefunction $\psi_0^{(0)}$ and the optimized first-order correction function $\psi_0^{(1)}$ in a quartic oscillator ($\lambda=0.1$).

with available results (0.5591 a.u. in our FGH calculation) showing the usefulness of the present method of computing $\psi_n^{(1)}$.

### 4.3. Application to more complex problems: RSPT for He-atom

The algorithm can be applied to more complex problems without any special difficulty. Let us consider the case of the He-atom in the ground $(S_0^1)$ state which can be described by the following partitioning of the Hamiltonian:

$$H(r_1,r_2) = h_0(r_1) + h_0(r_2) + \frac{1}{r_{12}}$$

$$= H_0(r_1,r_2) + \frac{1}{r_{12}}$$

$$\text{where } \frac{1}{r_{12}} = V(r_1,r_2)\,. \tag{23}$$

$h_0(r_i)$ is the Hamiltonian of the $i$th electron in the Coulomb field of the helium nucleus (nuclear charge $= z$). The unperturbed ground-state $\psi_0^0(r_1,r_2)$ is given by

$$\psi_0^0(r_1,r_2) = N\,\mathrm{e}^{-z(r_1+r_2)/2}, \ldots (z=2) \tag{24}$$

and the first-order perturbation correction to $\psi_0^0(r_1,r_2)$ can be obtaibed by solving the equation

$$\left[H_0(r_1,r_2) - E_0^0\right]\psi_0^{(1)}(r_1,r_2)$$

$$= \left\{\langle \psi_0^0(r_1,r_2) \mid V(r_1,r_2) \mid \psi_0^0(r_1,r_2)\rangle - V(r_1,r_2)\right\}\psi_0^0(r_1,r_2)\,. \tag{25}$$

Just as before, $\psi_0^{(1)}(r_1,r_2)$ can be represented by a string of floating-point numbers which represent the amplitude of $\psi_0^{(1)}(r_1,r_2)$ at different points in space. It can be handled either as a 1-d string or a 2-d array of numbers. A suitable definition of crossover and mutation operators (depending upon the mode of representation) then suffices for application of GA to the solution of Eq. (24). Fig. 5 shows how the fitness of the best string has evolved in this case over different generations. The energy corresponding to the best string turns out to be $-2.77877$ a.u. which is not bad considering the rather crude wavefunction we started with. We could do better by choosing $\psi_0^0(r_1,r_2) = N\mathrm{e}^{-z'(r_1+r_2)/2}$ where $z'$ is the screened nuclear charge, the optimum value of $z'$ being equal to $27/32$. $H(r_1,r_2)$ of Eq. (23) can then be repartitioned as follows, defining a new $H_0(r_1,r_2)$ and $V(r_1,r_2)$ consistent with the new choice of $\psi_0(r_1,r_2)$:

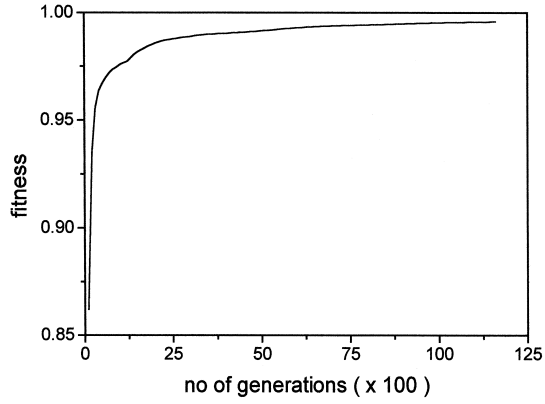


Fig. 5. The fitness of the best string is shown against the number of generations elapsed during direct calculation of $\psi^1$ for the ground state of the He-atom.

$$H(r_1,r_2) = h_0'(r_1) + h_0'(r_2) + \left\{\frac{(z'-2)}{r_1} + \frac{(z'-2)}{r_2}\right\} + \frac{1}{r_{12}}$$

$$= H_0'(r_1,r_2) + V'(r_1,r_2)\,, \tag{26}$$

where $h_0'(r_1)$ or $h_0'(r_2)$ represents a hydrogenic Hamiltonian with $z = 27/32$ instead of 2. When the calculations are repeated with the new $H_0'$, $\psi_0'$ and $V'$ the perturbative estimate of the energy eigenvalue obtained from the solution of the first-order equation turns out to be $-2.8712$ a.u. which is close to the $s$-limit energy of the He-atom. For atoms with larger number of electrons, it would be more advantageous to use a zeroth-order Hamiltonian constructed from a mean-field theory [1] and solve the corresponding perturbation equations by the method proposed here. In general, if the interacting many-particle problem can be reduced to an effective one-particle Schrödinger equation, GA can be used profitably to solve it directly leading to the generation of numerical

basis sets of high quality which can be used later for perturbative calculations.

## 5. Conclusions

GA-based strategies can be used successfully to solve the energy eigenvalue equation for a single particle directly or to solve the inhomogeneous differential equations of RSPT. The method is basis set free and handles homogeneous and inhomogeneous differential equations on the same footing while solving the Schrödinger equation directly by GA. $\psi_n$ and $E_n$ are calculated simultaneously and conveniently as opposed to what is normally done in a finite difference approach to the eigenvalue problem. In the second case both $\psi_n^{(1)}$ and $\psi_n^{(2)}$ can be obtained easily and accurately. The algorithm provides a stable and general alternative to standard numerical integration and has the advantage that it can handle constraints. The higher-order correction functions $\psi_n^{(m)}(m > 2)$ can be similarly obtained. $\psi_n^{(m)}$ obtained directly can provide useful information about other properties of the system without having to use sum-over-states expressions in a finite basis space. The method can handle two-particle problems with facility and is extendable to many-particle systems through a mean-field route. However, many more applications and further refinement of the strategy of implementing GA for solving the Schrödinger equation may be necessary before the present method can generally compete with the currently available methods in terms of cost-effectiveness.

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## References

[1] J.O. Hirschfelder, W. Byers Brown, S.T. Epstein in: P.O. Löwdin (Ed.), Adv. Quantum. Chem. 1 (1964) 255.
[2] A. Dalgarno, J.T. Lewis, Proc. Roy. Soc. A 223 (1955) 70.
[3] A. Dalgarno, J.T. Lewis, Proc. Phys. Soc. (Lond.) A69 (1956) 57.
[4] C. Schwartz, Ann. Phys. (NY) 6 (1959) 156.
[5] D.E. Goldberg, Genetic Algorithms in Search, Optimization and Machine Learning, Addison–Wesley, Reading, MA, 1989.
[6] F. Hoffmeister, T. Back, Genetic Algorithms and Evolution Strategies, in: H.P. Schwefel, R. Männer (Ed.), Proceedings of the First International Conference on Parallel Problem Solving from Nature (PPSN), Dortmund, Germany, 1990.
[7] K.A. De Jong, Learning with Genetic Algorithm: An overview, in: Machine Learning, vol. 3, 1988, pp. 121–138.
[8] H.A. Kramers, Quantum Mechanics, Dover, New York, 1964, p. 192.
[9] A.V. Sergeev, A.I. Sherstyuk, Zh. Eksp. Teor. Fiz. 82 (1982) 1070 [Sov. Phys. JETP 55 (1982) 625].
[10] I.D. Feranchuk, L.I. Komarov, J. Phys. A 17 (1984) 3111.
[11] F.J. Rogers, H.C. Graboske Jr., D.J. Harwood, Phys. Rev. A1 (1970) 1577.
[12] K.M. Roussel, R.F. O'Connell, Phys. Rev. A9 (1974) 52.
[13] J. Killingbeck, J. Phys. A 14 (1981) 1005.
[14] C.C. Marston, G.G. Balint-Kurti, J. Chem. Phys. 91 (1989) 6.
[15] P. Dutta, S. Adhikari, S.P. Bhattacharyya, Chem. Phys. Lett. 212 (1992) 677.