Quantum confinement in 1D systems through an imaginary-time evolution method

Amlan K. Roy∗

Department of Chemical Sciences, Indian Institute of Science
Education and Research Kolkata, Mohanpur, Nadia, 741246, India.

Abstract

Quantum confinement is studied by numerically solving time-dependent Schrödinger equation. An imaginary-time evolution technique is employed in conjunction with the minimization of an expectation value, to reach the global minimum. Excited states are obtained by imposing the orthogonality constraint with all lower states. Applications are made on three important model quantum systems, namely, harmonic, repulsive and quartic oscillators; enclosed inside an impenetrable box. The resulting diffusion equation is solved using finite-difference method. Both symmetric and asymmetric confinement are considered for attractive potential; for others only symmetrical confinement. Accurate eigenvalue, eigenfunction and position expectation values are obtained, which show excellent agreement with existing literature results. Variation of energies with respect to box length is followed for small, intermediate and large sizes. In essence a simple accurate and reliable method is proposed for confinement in quantum systems.

Keywords: Imaginary-time evolution, diffusion equation, quantum confinement, harmonic oscillator, inverted oscillator, quartic potential.

∗ Email: akroy@iiserkol.ac.in, akroy6k@gmail.com, Ph: +91-3473-279137, Fax: +91-33-25873020.
I. INTRODUCTION

Ordinarily in usual stationary-state problem within quantum mechanics, a constraint is imposed on wave function that it should vanish at infinity. However, in some cases, it may be desirable to consider a bounded or enclosed system by requiring that the same vanishes on surface of a finite region of space. Such confinement situation in a quantum system was first attempted in 1937 \cite{1} to model the effects of pressure on energy, polarizability and ionization potential of hydrogen atom inside a spherically impenetrable cavity. This was followed by the works of \cite{2}, where solution of a spherically confined hydrogen atom (CHA) was reported using confluent hyper-geometric functions. Properties of a confined quantum system (such as many-electron atom or molecule) differ substantially from their free or unconfined counterparts. In recent years, models of quantum objects spatially confined by different external potentials have received tremendous attention from various areas of physics, chemistry and biology. Practical applications include atoms, molecules trapped inside cavities, zeolite channels or hollow cages of carbon-based nanomaterials such as endohedral fullerenes; neutral, charged donors in semiconductor wells; excitons enclosed in quantum dots; artificial atoms, etc. They are also used as important models for vibronic spectra of point defects, impurities or luminescence in solids, magnetic properties of electron gas in semiconductor nanostructures, thermodynamic properties of non-ideal gases, partially ionized plasmas, etc. Further, they also hold promise for potential applications in circuit devices of nano and molecular sizes including quantum computers. The literature is vast; some of these could be found in following elegant references, \cite{3,4,5}.

Two most prominent systems on which quantum confinement studies have been made most extensively are: 3D confined harmonic oscillator (CHO) and CHA. Variation of energy, eigenfunction, spatial expectation values with respect to the box size of a CHO, inside an impenetrable spherical cavity, was investigated by a wide range of theoretical methodologies, \textit{viz.}, hypervirial treatment, Padé approximation, variational theory, WKB method, supersymmetric approach, proper quantization rule, generalized pseudospectral (GPS) method, etc., \cite{6,7,8,9,10}. Many interesting phenomena occur in this case. For example, the characteristic degeneracy of \textit{free} isotropic harmonic oscillator is removed; equal energy separation between two successive levels of respective free system disappears; a new kind of \textit{accidental degeneracy} emerges whereby, for a particular radius of confinement, energies of two CHO states...
coincide, and many others. Likewise, for CHA, an enormous amount of work exists to study numerous properties like energy, pressure, dynamic polarizability, hyperfine splitting constant, dipole shielding factor, excited-state life time, density derivative at the nucleus, etc. A vast array of methodologies are proposed; some notable ones are perturbation method, Padé approximation, WKB method, hypervirial theorem, Hartree-Fock self-consistent with Slater-type orbital bases, variational method, super-symmetric approach, Lie-algebraic treatment, asymptotic iteration method, GPS, etc., [11–17]. An interesting aspect is that, binding energy of a CHA decreases as confining radius decreases, becoming zero at a certain critical radius. For various other features, consult the references and therein.

In this work, we are interested in confinement of a few selected 1D systems, viz., linear isotropically confined harmonic oscillator (CHO), quartic and inverted oscillator. The former was studied by a number of workers employing a variety of techniques. In some of the oldest attempts [18, 19], effect of finite boundaries on energy levels was reported in terms of confluent hyper-geometric functions. Later it was followed up in [20], who advocated a semi-classical WKB method and found that eigenvalues reduce to respective unbounded oscillator values if classical turning points are inside the potential enclosure and not near the walls. Also, they become plane-wave box eigenvalues when the separation of turning points is large compared to the size of box. Subsequently, a series analytical solution [21] was offered for eigenvalues by restricting center of oscillator at the center of potential cavity. Eigenvalues were numerically presented as roots of a polynomial as well [22]. Padé approximants constructed as interpolations between perturbative and asymptotic solutions were proposed in [23]. Diagonal hypervirial relations [24] as well as hypervirial perturbative method [25] were proposed. Approximate wave functions were constructed as linear combination of two-term even and odd polynomials [26]. Multi-well polynomial oscillators were treated by a Rayleigh-Ritz variational method with a trigonometric basis set [27]. Numerical solutions were offered which converge to corresponding unbounded solutions, in the norm of Hilbert space [28]. CHA and confined quartic oscillators were investigated by means of WKB and modified airy function method [29]. Highly accurate eigenvalues for \(N\)-dimensional CHO were published in [9] by finding the zeros of hyper-geometric function numerically. Eigenvalues and Einstein coefficients were obtained by power-series method [30], perturbation methods [31]. Coherent states associated with CHO in 1D were examined as well [32].

All the above works deal with symmetric confinement however, and studies on asym-
metric confinement has been rather very few. For example, energy spectrum and Einstein coefficients in asymmetric CHO were offered by a power series method \cite{30}, a perturbative approach \cite{33}. Along with the symmetric confinement, we pay special attention to asymmetric case here. Another interesting candidate for confinement is inverted (or repulsive) oscillator. Both harmonic and inverted oscillator potentials are produced simultaneously inside an ideal Penning trap to confine charged particles \cite{34}. Although these two oscillators are mathematically very much alike in the sense that solutions of one can be obtained almost directly from other, there are important physical differences between the two. Thus, while a free harmonic oscillator offers discrete, equidistant, non-degenerate energy spectrum with square-integrable wave functions, latter gives rise to doubly-degenerate continuous energies whose eigenfunctions are not square-integrable. The latter has important applications in instability model, 2D string theory, a model for early time evolution, etc., \cite{35}. Many other characteristic features including time-dependent (TD) extensions could be found in references \cite{35, 36}. However, only two attempts are known so far for their confinement, viz., an algebraic approach \cite{37}, a Padé approximation of perturbative and asymptotic solution \cite{23}. In this work, we make an attempt to understand confinement in this system as well.

Our methodology is based on an imaginary-time propagation (ITP) scheme, which provides accurate bound-state solutions by transforming the TD Schrödinger equation (SE) in imaginary time into a diffusion equation. The latter is solved numerically in conjunction with a minimization of energy expectation value to hit the global minimum. This procedure was initially proposed several decades ago and thereafter was successfully applied to a number of systems invoking several different implementation schemes \cite{38–44}. The present implementation has been successfully used in a few free systems, such as ground states in atoms, diatomic molecules within a quantum fluid dynamical density functional theory \cite{45, 46}, low-lying states in harmonic, anharmonic potentials in 1D, 2D, as well as spiked oscillator \cite{47–51}. However, this scheme has never been attempted in confinement situations. Thus the main objectives of this communication are two-fold: (i) to assess the performance and feasibility of ITP method in the context of confinement, which can broaden its regions of applicability (ii) to study the energy spectrum of mentioned potentials under confinement in terms of ground- and excited-state wave functions, energies, expectation values with particular emphasis on asymmetrical confinement and inverted oscillator. Comparison with literature results are made wherever possible. The paper is organized as follows: Section II
II. THE ITP METHOD FOR A QUANTUM CONFINED SYSTEMS

In this section, we give an overview of the ITP method as employed here for a particle under confinement. More complete account could be found in the references [45–51]. Our starting point is TDSE, which for a particle under the influence of a potential \( V(x) \) in 1D, is given by (atomic unit employed unless otherwise mentioned),

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \psi(x,t) = H \psi(x,t) = \left[ -\frac{1}{2} \frac{d^2}{dx^2} + v(x) + v_c(x) \right] \psi(x,t). \tag{1}
\]

Hamiltonian operator contains the usual kinetic and potential energy operators. This method is, in principle, exact. Here and in following sections, equations are given for 1D problems; extension to higher dimension is straightforward (see e.g., [50] for application in 2D). This work considers effect of finite boundaries in three 1D potentials, viz., \( v(x) = \pm \frac{1}{2}x^2 \) or \( v(x) = \frac{1}{2}x^4 \), corresponding to harmonic, repulsive, quartic oscillators respectively. Last term is introduced to produce the effect of confinement by centrally enclosing the oscillator inside two infinitely high, hard impenetrable walls (for asymmetric confinement, see later),

\[
v_c(x) = \begin{cases} 
0, & -R < x < +R \\
\infty, & |x| \geq R.
\end{cases} \tag{2}
\]

Equation (1) can be written in imaginary time, \( \tau = it \) (\( t \) is real time) to obtain a non-linear diffusion-type equation resembling a diffusion quantum Monte Carlo equation [52],

\[
- \frac{d\psi(x,\tau)}{d\tau} = H\psi(x,\tau). \tag{3}
\]

One can write its formal solution as,

\[
\psi(x,\tau) = \sum_{k=0}^{\infty} c_k \psi_k(x) \exp(-\epsilon_k \tau). \tag{4}
\]

If the initial guessed wave function \( \psi(x,\tau) \) at \( \tau = 0 \), is propagated for a sufficiently long time, it will converge towards the desired stationary ground-state wave function; \( \lim_{\tau \to \infty} \psi(x,\tau) \approx c_0 \psi_0(x) e^{-\epsilon_0 \tau} \). Thus, provided \( c_0 \neq 0 \), apart from a normalization constant, this leads to the global minimum corresponding to an expectation value \( \langle \psi(x,\tau)|H|\psi(x,\tau) \rangle \).
The numerical solution of Eq. (3) can be obtained by using a Taylor series expansion of \( \psi(x, \tau + \Delta \tau) \) around time \( \tau \) as follows,

\[
\psi(x, \tau + \Delta t) = e^{-\Delta \tau H} \psi(x, \tau). \tag{5}
\]

Here, exponential in right-hand side refers to the time-evolution operator, which propagates diffusion function \( \psi(x, \tau) \) at an initial time \( \tau \) to an advanced time step to \( \psi(x, \tau + \Delta \tau) \). Since this is a non-unitary operator, normalization of the function at a given time \( \tau \) does not necessarily preserve the same at a future time \( \tau + \Delta \tau \). Transformation of Eq. (5) into an equivalent, symmetrical form leads to \((j, n\) signify space, time indices respectively),

\[
e^{(\Delta \tau/2)H_j} \psi_j^{(n+1)} = e^{-(\Delta \tau/2)H_j} \psi_j^n. \tag{6}
\]

A prime is introduced in above equation to indicate the \textit{unnormalized} diffusion function. Taking the full form of Hamiltonian from Eq.(1), one can further write,

\[
e^{(\Delta \tau/2)\left[ -\frac{1}{2}D_x^2 + v(x_j) \right]} \psi_j^{(n+1)} = e^{-(\Delta \tau/2)\left[ -\frac{1}{2}D_x^2 + v(x_j) \right]} \psi_j^n, \tag{7}
\]

where the spatial second derivative has been defined as \( D_x^2 = \frac{d^2}{dx^2} \). Now, expanding the exponentials on both sides, followed by truncation after second term and approximation of second derivative by a five-point difference formula \([53]\) \((\Delta x = h)\) leads to,

\[
D_x^2 \psi_j^n \approx \frac{-\psi_{j-2}^n + 16\psi_{j-1}^n - 30\psi_{j}^n + 16\psi_{j+1}^n - \psi_{j+2}^n}{12h^2}, \tag{8}
\]

yields a set of \( N \) simultaneous equations, as follows,

\[
\alpha_j \psi_{j-2}^{(n+1)} + \beta_j \psi_{j-1}^{(n+1)} + \gamma_j \psi_j^{(n+1)} + \delta_j \psi_{j+1}^{(n+1)} + \zeta_j \psi_{j+2}^{(n+1)} = \xi_j^n. \tag{9}
\]

After some straightforward algebra, the quantities \( \alpha_j, \beta_j, \gamma_j, \delta_j, \zeta_j, \xi_j^n \) are identified as,

\[
\alpha_j = \zeta_j = \frac{\Delta \tau}{48h^2}, \quad \beta_j = \delta_j = -\frac{\Delta \tau}{3h^2}, \quad \gamma_j = 1 + \frac{5\Delta \tau}{8h^2} + \frac{\Delta \tau}{2} v(x_j), \tag{10}
\]

\[
\xi_j^n = \left[ -\frac{\Delta \tau}{48h^2} \right] \psi_{j-2}^n + \left[ \frac{\Delta \tau}{3h^2} \right] \psi_{j-1}^n + \left[ 1 - \frac{5\Delta \tau}{8h^2} - \frac{\Delta \tau}{2} v(x) \right] \psi_j^n + \left[ -\frac{\Delta \tau}{48h^2} \right] \psi_{j+2}^n.
\]

Discretization and truncation occur on both sides; hence there may be some cancellation of errors. Here, \( \psi_j^{(n+1)} \) denotes unnormalized diffusion function at time \( \tau_{n+1} \) at various spatial grid points. Quantities like \( \alpha_j, \beta_j, \gamma_j, \delta_j, \zeta_j \) are expressed in terms of space and time spacings; the potential term appears only in \( \gamma_j \) and \( \xi_j^n \). The latter also requires knowledge of normalized diffusion functions \( \psi_{j-2}^n, \psi_{j-1}^n, \psi_j^n, \psi_{j+1}^n, \psi_{j+2}^n \) at spatial grids \( x_{j-2}, x_{j-1}, x_j, x_{j+1}, x_{j+2} \).
at a previous time $\tau_n$. This equation can be further recast in a convenient pentadiagonal matrix form as follows,

$$
\begin{bmatrix}
\gamma_1 & \delta_1 & \zeta_1 \\
\beta_2 & \gamma_2 & \delta_2 & \zeta_2 \\
\alpha_3 & \beta_3 & \gamma_3 & \delta_3 & \zeta_3 \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
\alpha_{N-1} & \beta_{N-1} & \gamma_{N-1} & \delta_{N-1} & \zeta_{N-2} \\
(0) & \alpha_N & \beta_N & \gamma_N \\
\end{bmatrix}
\begin{bmatrix}
\psi_1^{(n+1)} \\
\psi_2^{(n+1)} \\
\psi_3^{(n+1)} \\
\vdots \\
\psi_{N-2}^{(n+1)} \\
\psi_{N-1}^{(n+1)} \\
\psi_N^{(n+1)} \\
\end{bmatrix}
= 
\begin{bmatrix}
\xi_1^n \\
\xi_2^n \\
\xi_3^n \\
\vdots \\
\xi_{N-2}^n \\
\xi_{N-1}^n \\
\xi_N^n \\
\end{bmatrix}.
$$

This matrix equation can be easily solved for $\{\psi_j^{(n+1)}\}$ using standard routine, e.g., satisfying the boundary condition $\psi_j^n = \psi_{N}^n = 0$, at all time. Thus, starting from an initial guessed function $\psi_j^0$ at $n = 0$ time step, the diffusion function is propagated according to Eq. (4) following the sequence of steps as outlined above. Then at a given time level ($n+1$), the next series of instructions are performed, viz., (a) normalization of $\psi_j^{(n+1)}$ to $\psi_j^{(n+1)}$ (b) if an excited state calculation is intended, then $\psi_j^{(n+1)}$ needs to be orthogonalized to all lower states (the present work employs Gram-Schmidt method) (c) desired expectation values are calculated as $\epsilon_0 = \langle \psi_j^{(n+1)} | H | \psi_j^{(n+1)} \rangle$ (d) difference in expectation values between two successive time steps, $\Delta \epsilon = \langle H \rangle^{(n+1)} - \langle H \rangle^n$, is monitored (e) until $\Delta \epsilon$ reaches below a certain prescribed tolerance limit, one proceeds with the calculation at next time level $\psi_j^{(n+2)}$ iteratively. The trial functions for even and odd states were selected as simple Gaussian functions such as $e^{-x^2}$ and $xe^{-x^2}$ respectively. Various integrals were evaluated by means of standard Newton-Cotes quadratures.

**III. RESULTS AND DISCUSSION**

Before considering general confinement situation, at first, however, it may be prudent to illustrate the convergence of ITP results with respect to grid parameters for some sample cases. For this purpose, Table I gives our obtained ground-state energies for attractive quadratic potential when confined within hard walls of different sizes; viz., $R = 0.5$ (small box) and 5 (large box). Note that all entries in this and following tables are given in atomic units unless otherwise stated; also the reported quantities are truncated instead of rounded-off. Moreover, all calculations employ quadrupole precision. As evident, one can
### TABLE I. Convergence of energies of the attractive oscillator with respect to grid parameters.

| $N$  | $h$   | Energy† | $N$  | $h$   | Energy‡ |
|------|-------|---------|------|-------|---------|
| 101  | 0.01  | 4.9511318915149 | 101  | 0.1   | 0.5000460006214 |
| 201  | 0.005 | 4.9511294838148 | 201  | 0.05  | 0.5000029108342 |
| 501  | 0.002 | 4.9511293273648 | 501  | 0.02  | 0.500000748503 |
| 1001 | 0.001 | 4.9511293235110 | 1001 | 0.01  | 0.500000047530 |
| 1601 | 0.000625 | 4.951129323933 | 1601 | 0.00625 | 0.50000007909 |
| 2001 | 0.0005 | 4.951129323702 | 2001 | 0.005 | 0.50000003096 |
| 4001 | 0.00025 | 4.9511293232551 | 4001 | 0.0025 | 0.50000000955 |
| 5001 | 0.0002 | 4.9511293232545 | 5001 | 0.002 | 0.50000000846 |
| 8001 | 0.000125 | 4.9511293232542 | 8001 | 0.00125 | 0.50000000782 |
| 10001 | 0.0001 | 4.9511293232541 | 10001 | 0.001 | 0.50000000768 |
| 20001 | 0.00005 | 4.9511293232541 | 20001 | 0.0005 | 0.50000000768 |

†Reference value is 4.9511293232541 [9, 30].‡Reference value is 0.5000000000767 [9, 30].

produce reasonably good-quality results even for as small as 101 spatial grid points. However, adjusting grid spacings and points, energies could be systematically improved to attain very good accuracy, if desired. Qualitatively similar conclusions hold for other instances.

Now, energy levels of a 1D CHO in an impenetrable box is presented. For a symmetrical box of size $2R$, the boundary conditions on wave functions are: $\psi(x = -R) = \psi(x = R) = 0$. Table II offers eigenvalues of six lowest states for 13 selected box lengths covering small, intermediate and large sizes of box. Since the potential energy is a symmetrical function in position space, the eigenstates possess definite odd and even parity. For very small box sizes, no results are available for direct comparison. For medium and larger box size, however, as already mentioned in Section I, a number of literature results exist. Some of the notable ones are quoted to facilitate comparison. For small box size and lower states, these are in good agreement with the result of [23]. In their calculation, dimension of the matrix varied with $R$; reported eigenvalues were obtained by employing $35 \times 35$ matrices. Later, more precise energies were offered in [30] and [9]. Decent results were also provided in [33] through perturbation theory. Our present results either completely match with these reference values or show very slight deviation. It is interesting to note that for smaller box, kinetic energy increases very sharply (since it is inversely proportional to square of $R$) dominating over the quadratic potential. Thus in this situation, eigenenergy has maximum contribution from the former; energy spectrum more closely resembles a “free particle in a
TABLE II. Variation of ground- and excited-state \((n = 0 - 5)\) energies of attractive potential confined in an impenetrable box of various size. PR implies Present Result.

| R   | \(E_0\) (PR) | \(E_0\) (Literature) | \(E_1\) (PR) | \(E_1\) (Literature) |
|-----|--------------|-----------------------|--------------|-----------------------|
| 0.1 | 123.37070846785 | 493.48163341761 | 78.955668595686 |
| 0.25 | 19.74329750279 | 493.48163341761 | 78.955668595686 |
| 0.5 | 4.9511293232541 | 4.9511293232541 | 4.951129323264 | 4.951129323264 |
| 0.75 | 2.289871904328 | 8.8523841813955 | 5.0755820152267 | 5.0755820152267 |
| 1.0 | 1.298459831928a | 1.2984598319320b | 2.5049761785351 | 2.5049761785351 |
| 1.5 | 0.688931753647a | 5.0755820152267 | 5.0755820152267 | 5.0755820152267 |
| 3.0 | 0.50000000000768a | 0.500000000007688b | 1.5000000036715 | 1.5000000036715 |
| 4.5 | 0.50000000000768 | 0.50000000000768 | 1.5000000036715 | 1.5000000036715 |

\(^a\)Ref. [23]. \(^b\)Ref. [30]. \(^c\)Ref. [9].

box” problem than than that of an unconfined harmonic oscillator. However, as box size increases, lower energy levels become similar to those of free harmonic oscillator, but the higher energy levels remain similar to those of free particle in a box \[^{[33]}\]. For small box size \((R < 1.5)\), energy levels remain close to corresponding eigenvalues of free particle in a
TABLE III. Ground and excited-state \((n = 0 \sim 5)\) energies of repulsive potential confined in a 1D impenetrable box. Literature results are taken from \([23]\). PR implies Present Result.

| \(R\) | \(E_0\) (PR) | \(E_0\) (Ref.) | \(E_1\) (PR) | \(E_1\) (Ref.) | \(E_2\) (PR) | \(E_2\) (Ref.) |
|-------|-------------|---------------|-------------|---------------|-------------|---------------|
| 0.25  | 19.735124564890 | 19.73512456499 | 78.948001549339 | 78.94800154880 | 177.64316620104 | 177.6431662023 |
| 0.5   | 4.918456569838  | 4.918456569664 | 19.703865991252 | 19.70386599097 | 44.37436946295 | 44.37436946227 |
| 1.0   | 1.1677566722249 | 1.167756672152 | 4.7929066341410 | 4.792906633984 | 10.948019879701 | 10.9480198787 |
| 2.0   | 0.002263913456  | 0.0022633913 | 0.6314643021773 | 0.63146430207 | 2.16835419540 | 2.1683544616 |
| 3.0   | −1.17047317507  | −1.17047317507 | −1.1508580516009 | −1.1508580516 | 0.2001065083248 | 0.2001065083248 |
| 4.0   | −3.7256132438955 | −3.725604475469 | −3.725604462280 | −3.725604462280 | −1.1822419664242 | −1.1822419664242 |
| 4.5   | −5.4320174048507 | −5.432017356665 | −2.4795880893709 | −2.4795880893709 | −10.698311519233 | −10.698311519233 |
| 5.0   | −7.4100334752198 | −7.4100334751181 | −7.4100334751181 | −7.4100334751181 | −4.1004783580571 | −4.1004783580571 |
| 5.5   | −9.6554493985902 | −9.6554493985902 | −9.6554493985902 | −9.6554493985902 | −13.451543619391 | −13.451543619391 |
| 6.0   | −14.937690072408 | −14.937690072408 | −14.937690072408 | −14.937690072408 | −10.698311519233 | −10.698311519233 |
| 6.5   | −17.9707348466966 | −17.9707348466966 | −17.9707348466966 | −17.9707348466966 | −13.451543619391 | −13.451543619391 |
| 7.0   | −24.81452848751  | −24.81452848751 | −24.81452848751 | −24.81452848751 | −19.765797720758 | −19.765797720758 |
| 8.0   | −41.589187578680 | −41.589187578680 | −41.589187578680 | −41.589187578680 | −35.570897876444 | −35.570897876444 |
| 10.0  | −710.60127614086 | −710.60127614086 | −710.60127614086 | −710.60127614086 | −42.44946699535 | −42.44946699535 |
| 10.0  | −30.831539208937 | −30.831539208937 | −30.831539208937 | −30.831539208937 | 7.101276140860 | 7.101276140860 |

box of same size; the harmonic oscillator, in this case, is just a perturbation. On the other hand, for \(R > 5\) or so, energies converge to that of the unconfined harmonic oscillator, as one expects. In fact, following a similar argument, 1D CHO has been proposed to serve as possibly one of the simplest examples of a two-mode system \([55]\). It consists of two exactly solvable limits, \(viz.,\) the 1D harmonic oscillator and particle in a 1D box, where each has its own characteristic spectral feature and represent two different excitation modes of system.

Next in Table III, first six eigenvalues of negative quadratic oscillator symmetrically constrained inside an impenetrable box are presented. Once again, we consider a variety of confining length including small, medium and large box sizes. As mentioned earlier,
FIG. 1. Energy eigenvalues (a.u.) of six lowest states of (a) attractive and (b) repulsive harmonic oscillators under symmetrical confinement between two hard walls.

attempts for bounded inverted oscillator has been rather much less compared to its attractive counterpart. Only one result could be found, which is quoted. While our energies, in general, show good agreement with these literature values, considering the performance of this approach here and several other previous works, we believe that present results are more accurate than the reference. Literature energies seem to be better for smaller box length; quality worsens as the same increases. It is gratifying that uniformly accurate energies are obtained irrespective of the length of enclosure or state index. The positive, non-degenerate eigenvalues at smaller \( R \) become negative, doubly degenerate as the same increases.

Above energy variations of Tables II, III are graphically reproduced in Fig. 1. Left panel (a) depicts lowest six eigenvalues for boxed-in symmetrical CHO with respect to function of box size, while right panel (b) gives those for an enclosed repulsive oscillator confined symmetrically. In CHO case, eigenvalues monotonically decrease at first and then attain the constant energy of unbounded QHO. Moreover the states never cross each other; no mixing among these occur at any confining size. As the confinement length is decreased, energy increases rapidly. Energy levels of confined negative parabolic potential sharply increases at smaller \( x_c \). Like the attractive counterpart, in this occasion also, energy levels do not mix when box size is smaller and there is no degeneracy. Starting from high positive values, these energies fall continuously passing through zero. As \( x_c \) increases, eventually eigenvalues assume negative values and become doubly degenerate. Additionally Table IV now offers
TABLE IV. Position expectation values (a.u.) of confined attractive (left) and repulsive (right) oscillators for lowest three states. Numbers in the parentheses refer to literature results [9].

| R  | n  | \langle x^2 \rangle | \langle x^4 \rangle | \langle x^2 \rangle | \langle x^4 \rangle |
|----|----|----------------------|----------------------|----------------------|----------------------|
| 0.5| 0  | 0.032635763 (0.032635761) | 0.002564116 (0.002564116) | 0.032709794 | 0.002573249 |
|    | 1  | 0.007236536 | 0.007124052 | 0.00703962 | 0.007135575 |
| 2  | 0  | 0.077117086 | 0.009874996 | 0.077696797 | 0.009876561 |
| 5.0| 0  | 0.499999999 (0.499999999) | 0.749999999 (0.749999997) | 17.9714491 | 331.396244 |
|    | 1  | 1.499998872 | 3.74999353 | 17.9714491 | 331.396244 |
|    | 2  | 2.499997316 | 9.74996153 | 12.9561193 | 190.3396244 |

two position expectation values \( \langle x^2 \rangle, \langle x^4 \rangle \) for symmetrically confined quadratic potential, having both positive and negative coupling constants. These are given for two confinement lengths in case of three lowest states. To the best of our knowledge, only the result of [9] is available for ground states in attractive potential. Present results compare quite favorably with these values. As box length increases, slight disagreement is noticed between these two. The double degeneracy of inverted oscillator with increasing \( R \) manifests in \( \langle x^2 \rangle \) and \( \langle x^4 \rangle \) becoming completely identical for first two states.

Now we consider the case of a 1D harmonic oscillator constrained asymmetrically inside an impenetrable box. To facilitate comparison with literature works, here we adopt the notation of [24, 30, 33]. Thus the respective time-independent SE is given as:

\[
-\frac{1}{2} \frac{d^2 \psi}{dx^2} + \frac{1}{2} (x - d)^2 \psi + V(x) \psi = E \psi,
\]

where the effect of confinement is introduced as follows: \( V(x) = +\infty \), for \( |x| \geq R \) and \( V(x) = 0 \), when \( |x| < R \). It represents an infinite square well of width 2\( R \) with \( d \) signifying position of minimum in the potential. Following qualitative energy spectrum was observed in WKB analysis [20] long times ago: for low-lying states where classical turning points remain inside wall, \( E_n \cong (n + \frac{1}{2}) \), whereas in highly excited states where classical turning points are positioned well outside box, \( E_n \cong [(n + 1)^2 \pi^2] / R^2 \). Table V presents energies of ground and first five excited states of an asymmetrically confined harmonic oscillator along with some literature results. The size of our box is \( b - a = 2 \), while \( d = \frac{b + a}{2} \) and \( R = 1 \). Left and right walls are placed at \( a = -\frac{L}{2} + d, b = \frac{L}{2} + d \) respectively, where \( L = 2 \). These eigenvalues are given for a set of nine values of \( d \) covering a broad range. While the WKB [20] and hypervirial approach [24] produce qualitatively correct energies, results of [30] are significantly improved in this work. The ITP eigenvalues in general show good
TABLE V. Ground- and excited-state energies of asymmetrically confined harmonic oscillator.

| d    | E₀ (PR) | E₀ (Literature) | E₁ (PR) | E₁ (Literature) |
|------|---------|-----------------|---------|-----------------|
| 0.00 | 2.5969161464062 | 2.5969161464062 | 10.15114030453 | 10.15114030453 |
| 0.36 | 2.717763960504 | 2.717763960504 | 10.28314010610 | 10.28314010610 |
| 0.60 | 2.932632896411 | 2.932632896411 | 10.51755158073 | 10.51755158073 |
| 0.8 | 3.68687967275 | 3.6848973960275 | 11.338633919974 | 11.338633919974 |
| 1.08 | 4.2224833423893 | 4.2224833423893 | 11.924739350218 | 11.924739350218 |
| 1.32 | 6.08301956781 | 6.08301956781 | 13.9014458218 | 13.9014458218 |
| 1.92 | 9.1098673575 | 9.1098673575 | 17.23529572 | 17.23529572 |
| 2.64 | 11.012171537550 | 11.012171537550 | 19.294354690050 | 19.294354690050 |
| 3.00 | 14.66128653684 | 14.66128653684 | 22.583579507459 | 22.583579507459 |
| 3.50 | 21.6561526965 | 21.6561526965 | 39.799393003660 | 39.799393003660 |
| 4.0 | 22.648848775502 | 22.648848775502 | 39.92998488830 | 39.92998488830 |
| 4.6 | 22.882087130439 | 22.882087130439 | 40.162146552037 | 40.162146552037 |
| 5.0 | 23.698410538121 | 23.698410538121 | 40.97413938289 | 40.97413938289 |
| 5.5 | 24.814882372340 | 24.814882372340 | 41.55518734261 | 41.55518734261 |
| 6.0 | 26.249310409373 | 26.249310409373 | 43.513981920357 | 43.513981920357 |
| 6.6 | 29.572519377757 | 29.572519377757 | 46.822273977476 | 46.822273977476 |
| 7.0 | 31.67498542168 | 31.67498542168 | 48.8681835865 | 48.8681835865 |
| 7.5 | 34.91661131484 | 34.91661131484 | 52.14298363178 | 52.14298363178 |

| E₂ (PR) | E₂ (Literature) | E₃ (PR) | E₃ (Literature) |
|---------|-----------------|---------|-----------------|
| 0.00 | 22.517651562965 | 22.517651562965 | 39.799393003660 | 39.799393003660 |
| 0.36 | 22.6484875502 | 22.6484875502 | 39.92998488830 | 39.92998488830 |
| 0.60 | 22.882087130439 | 22.882087130439 | 40.162146552037 | 40.162146552037 |
| 0.8 | 23.698410538121 | 23.698410538121 | 40.97413938289 | 40.97413938289 |
| 1.08 | 24.814882372340 | 24.814882372340 | 41.55518734261 | 41.55518734261 |
| 1.32 | 26.249310409373 | 26.249310409373 | 43.513981920357 | 43.513981920357 |
| 1.92 | 29.572519377757 | 29.572519377757 | 46.822273977476 | 46.822273977476 |
| 2.64 | 31.67498542168 | 31.67498542168 | 48.8681835865 | 48.8681835865 |
| 3.00 | 34.91661131484 | 34.91661131484 | 52.14298363178 | 52.14298363178 |
| 3.50 | 37.15672311936 | 37.15672311936 | 55.49081774747 | 55.49081774747 |
| 4.0 | 39.408824563149 | 39.408824563149 | 62.904962222882 | 62.904962222882 |
| 4.6 | 41.66128653684 | 41.66128653684 | 66.23529572 | 66.23529572 |
| 5.0 | 43.91661131484 | 43.91661131484 | 71.05632112658 | 71.05632112658 |
| 5.5 | 46.1720542168 | 46.1720542168 | 74.322867045677 | 74.322867045677 |

aRef. 20. bRef. 24. cRef. 30. †PR implies Present Result.

agreement with above mentioned literature values, but are expected to be more accurate. For large asymmetry and higher states, first two reference energies tend to deviate more from respective correct values. No results could be found for last two states for direct comparison.

Finally some sample eigenvalues are given for pure quartic potential, viz., $V(x) = \frac{1}{2}x^4$, centrally located inside a hard impenetrable box in Table VI. Four states are presented at 9 selected $R$ values. As noticed, very few results are available for such system; these are quoted for easy referencing. First estimation of a bounded quartic oscillator was reported
TABLE VI. Ground and excited-state (n=0–3) energies of quartic oscillator confined in a 1D box.

| $R$ | $E_0$          | $E_1$          | $E_2$          | $E_3$          |
|-----|----------------|----------------|----------------|----------------|
| 0.1 | 123.37005706855| 493.48022575835| 1110.3305030230| 1973.9208889994|
| 0.25| 19.739289073204| 78.957058016652| 177.65318783303| 315.82768386638|
| 0.5 | 4.9360863901266 | 19.74273481544 | 44.418157501933 | 78.962323709406 |
| 1.0 | 1.2540984819831 | 4.9915845099650 | 11.182186655200 | 19.827026261394 |
|     | 1.2541$^a$,1.254097$^b$ | 4.9915845$^a$,4.9915835$^b$ | 11.1822$^a$,11.1821875$^b$ | 19.82702$^a$,19.82702$^b$ |
| 2.0 | 0.5363098872646 | 1.9412531887253 | 3.8918535694819 | 6.2917841208177 |
|     | 0.53631$^a$,0.4807965$^b$ | 1.94125$^a$,1.8375225$^b$ | 3.8918535$^a$,4.9144075$^b$ | 6.29178$^a$,6.336013$^b$ |
| 3.0 | 0.5301810699967 | 1.8998367873887 | 3.7278510725211 | 5.8223857288410 |
| 4.0 | 0.5301810452423 | 1.8998365149009 | 3.7278489689934 | 5.8223727556894 |
| 5.0 | 0.5301810452423 | 1.8998365149009 | 3.7278489689934 | 5.8223727556894 |
| 8.0 | 0.5301810452423$^\dagger$ | 1.8998365149009 | 3.7278489689934$^\ddagger$ | 5.8223727556951 |

$^a$Ref. [56]. $^b$Ref. [57]. $^\$It is an incorrect value. $^\dagger$Energy of unconfined oscillator is 0.530181045242 [27]. $^\ddagger$Energy of unconfined oscillator is 3.727848968993 [27].

Long times ago in [56]; compact recursion relations for power series coefficients of odd, even wave functions were obtained which were easily amenable to numerical computations through some iteration scheme. Later next year somewhat improved energies were published through a hypervirial perturbative approach [57]. Both these are available for all four states having box lengths 1 and 2. As observed in bounded harmonic oscillator, for a given $n$, eigenvalues increase in magnitude as the box is made smaller. The extent of this increase is larger as the box length is reduced. For even states, eigenvalues of corresponding unbounded oscillator were reported with very good accuracy in [27]; these authors employed a Rayleigh-Ritz variation method with trigonometric basis set. Note that their energies of Table 1 are quoted after dividing by a 2 factor. As observed, the energies of confined system readily converge to that of corresponding free systems. Lower states reach the energies of respective bound states for a smaller value of $R$ compared to higher states, which require a relatively larger $R$. According to [27], this critical distance for lowest two even states are estimated to be 5.5, which seems to be corroborated by our calculation.

IV. CONCLUSION

An imaginary-time evolution method has been employed to the problem of quantum confinement inside a hard impenetrable wall in 1D. Three important model potentials are chosen...
to demonstrate the validity and feasibility of our current approach, namely (a) harmonic (b) inverted and (c) quartic oscillator. While for all cases, we focus on symmetrical confinement, for (a), efforts are made to study asymmetrical situation as well. Many accurate reliable results have been reported for symmetrical confinement in (a); however for remaining two potentials and asymmetrical confinement in (a), there is a scarcity of good-quality reference works. In all these systems considered, present method offers results which are either comparable to best works known so far or surpasses the accuracy of all previous calculations. A detailed investigation is made on the variation of energy with respect to box size. Besides, position expectation values are presented, which also compare quite favorably with existing calculations. Both low and high-lying states have been considered for small, intermediate and large box size. Several states are reported here for the first time. The method is simple, accurate, easy to implement numerically and independent of basis sets. Further extension of the approach in other situations such as spherical confinement, higher dimensions and many-electron systems will strengthen its success, some of which may be taken up in future.

V. ACKNOWLEDGMENT

The author is grateful to the anonymous referee for kind constructive comments. It is a pleasure to thank Prof. Raja Shunmugam for his support.

[1] A. Michels, J. De Boer and A. Bijli, Physica 4, 981 (1937).
[2] A. Sommerfeld and H. Welker, Ann. Phys. 32, 56 (1938).
[3] W. Jaskólski, Phys. Rep. 271, 1 (1996).
[4] W. D. Heiss (Ed.) Quantum Dots: A Doorway to Nanoscale Physics, Springer, Berlin (2005).
[5] J. R. Sabin, E. Brändas and S. A. Cruz (Eds.) The Theory of Confined Quantum Systems, Parts I and II, Advances in Quantum Chemistry, Vols. 57, 58, Academic Press, Amsterdam (2009).
[6] N. Aquino, J. Phys. A 30, 2403 (1997).
[7] H. E. Montgomery Jr., N. Aquino and K. D. Sen, Int. J. Quant. Chem. 107, 798 (2007).
[8] S. M. Al-Jaber, Int. J. Theor. Phys. 47, 1853 (2008).
[9] H. E. Montgomery Jr., G. Campoy and N. Aquino, Phys. Scr. 81, 045010 (2010).
[10] A. K. Roy, Mod. Phys. Lett. A 29, 1450104 (2014).
[11] S. Goldman and C. Joslin, J. Phys. Chem. 96, 6021 (1992).
[12] N. Aquino, Int. J. Quant. Chem. 54, 107 (1995).
[13] C. Laughlin, B. L. Burrows and M. Cohen, J. Phys. B 35, 701 (2002).
[14] B. L. Burrows and M. Cohen, Int. J. Quant. Chem. 106, 478 (2006).
[15] N. Aquino, G. Campoy and H. E. Montgomery Jr., Int. J. Quant. Chem. 107, 1548 (2007).
[16] M. A. Shaqqor and S. M. Al-Jaber, Int. J. Theor. Phys. 48, 2462 (2009).
[17] H. Ciftci, R. L. Hall and N. Saad, Int. J. Quant. Chem. 109, 931 (2009).
[18] D. S. Kothari and F. C. Auluck, Sci. Cult. 6, 370 (1940).
[19] F. C. Auluck, Proc. Natl. Inst. Sci. India 7, 133 (1941).
[20] R. Vawter, Phys. Rev. 174, 749 (1968).
[21] R. Vawter, J. Math. Phys. 14, 1864 (1973).
[22] A. Consortini and B. R. Frieden, Nuovo Cimento B 35, 153 (1976).
[23] V. C. Aguilera-Navarro, E. Ley Koo and A. H. Zimerman, J. Phys. A 13, 3585 (1980).
[24] F. M. Fernández and E. Castro, Int. J. Quant. Chem. 20, 623 (1981).
[25] G. A. Arteca, S. A. Maluendes, F. M. Fernández and E. A. Castro, Int. J. Quant. Chem. 24, 1548 (2007).
[26] D. Keeports, Am. J. Phys. 58, 230 (1990).
[27] H. Taşeli, Int. J. Quant. Chem. 46, 319 (1993).
[28] R. Vargas, J. Garza and A. Vela, Phys. Rev. E 53, 1954 (1996).
[29] A. Sinha and R. Roychoudhury, Int. J. Quant. Chem. 73, 497 (1999).
[30] G. Campoy, N. Aquino and V. D. Granados, J. Phys. A 35, 4903 (2002).
[31] P. Amore and F. M. Fernández, Eur. J. Phys. 31, 69 (2010).
[32] M. Bagheri Harouni, R. Roknizadeh and M. H. Naderi, J. Phys. A 42, 045403 (2009).
[33] N. Aquino, E. Castaño, G. Campoy and G. Granados, Eur. J. Phys. 22, 645 (2001).
[34] D. J. Fernández and M. Velázquez, J. Phys. A 42, 085304 (2009).
[35] C. Yuce, A. Kilic and A. Coruh, Phys. Scr. 74, 114 (2006).
[36] D. Bermúdez and D. J. Fernández C. Ann. Phys. 333, 290 (2013).
[37] F. C. Rotbart, J. Phys. A 11, 2363 (1978).
[38] J. B. Anderson, J. Chem. Phys. 63, 1499 (1975).
[39] R. Kosloff and H. Tal-Ezer, Chem. Phys. Lett. 127, 223 (1986).
[40] L. Lehtovaara, J. Toivanen and J. Eloranta, J. Comput. Phys. **221**, 148 (2007).
[41] S. A. Chin, S. Janecek and E. Krotscheck, Chem. Phys. Lett. **470**, 342 (2009).
[42] I. W. Sudiarta and D. J. Wallace Geldart, J. Phys. A **42**, 285002 (2009).
[43] M. Strickland and D. Yager-Elorriaga, J. Comput. Phys. **229**, 6015 (2010).
[44] P. J. J. Luukko and E. Räsänen, Comput. Phys. Comm. **184**, 769 (2013).
[45] A. K. Roy, B. K. Dey and B. M. Deb, Chem. Phys. Lett. **308**, 523 (1999).
[46] A. K. Roy and S. I. Chu, J. Phys. B **35**, 2075 (2002).
[47] A. K. Roy, N. Gupta and B. M. Deb, Phys. Rev. A **65**, 012109 (2002).
[48] N. Gupta, A. K. Roy and B. M. Deb, Pramana-J. Phys. **59**, 575 (2002).
[49] A. Wadehra, A. K. Roy and B. M. Deb, Int. J. Quant. Chem. **91**, 597 (2003).
[50] A. K. Roy, A. J. Thakkar and B. M. Deb, J. Phys. A **38**, 2189 (2005).
[51] A. K. Roy, J. Math. Chem. **52**, 2645 (2014).
[52] B. L. Hammond, W. A. Lester Jr. and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry*, World Scientific, Singapore, (1994).
[53] M. Abramowitz and I. Stegun (Ed.) *Handbook of Mathematical Functions*, Dover, New York (1964).
[54] [http://www.math.uakron.edu/~kreider/anpde/Anpde.html](http://www.math.uakron.edu/~kreider/anpde/Anpde.html)
[55] V. G. Gueorguiev, A. R. P. Rau and J. P. Draayer, Am. J. Phys. **74**, 394 (2006).
[56] R. Barakat and R. Rosner, Phys. Lett. **83A**, 149 (1981).
[57] F. M. Fernández and E. A. Castro, Phys. Lett. **88A**, 4 (1982).