Excited state solver

Teemu Isojärvi

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1 Introduction

This is an improved version of my earlier GitHub code 'meanstate' [1], which allows for calculation of excited state wave functions of quantum systems without having to first solve all the lower energy eigenstates of $\hat{H}$ starting from the ground state. The method is designed to converge towards an eigenstate of $\hat{H}$ with energy closest to some given target value E_t. This can potentially save computation time, if only an excited state wave function and energy eigenvalue is needed without having to know the lower part of the spectrum. Instead of the R language, which the earlier program was made with, this one is made with C++ using the Google Canvas AI application as help when writing the code.

The application can solve eigenstates of the Hamiltonian for 1D or 2D single-particle systems with time-independent potential energy function $V(x)$ or $V(x, y)$.

2 Theory

To find the ground state $|0\rangle$ of a quantum system with Hamiltonian $\hat{H}$, the usual method is to start with a trial state vector $|\psi(0)\rangle$, with unknown spectral decomposition

$$|\psi(0)\rangle = C_1 |1\rangle + C_2 |2\rangle + C_3 |3\rangle + \ldots, \tag{1}$$

where $|k\rangle$ are the eigenstates of the Hamiltonian and C_k are complex-valued multipliers. The time evolution of this state is

$$|\psi(t)\rangle = C_1 e^{-iE_1 t} |1\rangle + e^{-iE_2 t} C_2 |2\rangle + e^{-iE_3 t} C_3 |3\rangle + \ldots, \tag{2}$$

when $\hat{H}$ is not a function of time and constants are set so that $\hbar = 1$. Changind to an imaginary time coordinate s, defined as $t = -is$, the state vector $|\psi(s)\rangle$ converges towards something with only a $|1\rangle$ component in the limit $s \to \infty$, as far as the trial vector $|\psi(0)\rangle$ has been chosen to be not orthogonal with $|1\rangle$.

To calculate the first excited state $|2\rangle$, this is done again with an initial state $|\psi(0)\rangle$ such that $\langle 2|\,\psi(0)\rangle \neq 0$ and simulating time propagation towards $s \to \infty$ while removing the $|1\rangle$ component from $|\psi(s)\rangle$ with a projection operator on every time step. This means that for an excited state calculation, approximations for all the lower energy eigenfunctions of $\hat{H}$ have to be computed first so that they can be eliminated from the state vector during imaginary time propagation.

The application presented here is based on forming an operator

$$\hat{A}(T) = \frac{1}{T}\int_0^T \hat{U}(\tau)d\tau = \frac{1}{T}\int_0^T \exp\left(-i\hat{H}\tau\right)d\tau, \tag{3}$$

which is the average of evolution operators $\hat{U}(t)$ for all time intervals t with $0 \leq t \leq T$.

If this operator is applied on a trial state vector $|\psi\rangle = C_1|1\rangle + C_2|2\rangle + \ldots$, the result is

$$\hat{A}^n|\psi\rangle = \frac{1}{T}\left[\frac{iC_1}{E_1}\left(e^{-iE_1t}-1\right)|1\rangle + \frac{iC_2}{E_2}\left(e^{-iE_2t}-1\right)|2\rangle + \ldots\right], \tag{4}$$

which is the average state vector on the evolution time interval of length T.

Operating on the vector $|\psi\rangle$ with $\hat{A}(T)$ n times, multipliers of E_k^{-n} accumulate in front of each term in the spectral decomposition. This means that unless the initial state vector $|\psi\rangle$ or the time interval T has been chosen really badly, the result should converge towards something that contains only the eigenstate of the Hamiltonian where energy is closest to value 0.

Forming the average evolution operator from a shifted Hamiltonian,

$$\hat{A}(T) = \frac{1}{T}\int_0^T \exp\left[-i(\hat{H}-E_t)\tau\right)d\tau, \tag{5}$$

where E_t is a trial energy value, the result should converge towards the eigenstate of $\hat{H}$ with energy closest to value E_t.

The C++ program here uses the Crank-Nicolson time stepping ([2]), and Alternating Direction Implicit method for 2D, to calculate the evolution of a given initial wave function and to find the average wave function on the time interval of length T. This is done for many iterations to try to approach the energy eigenvalue closest to the target energy E_t.

In the source code, the iteration lenths T, time step δt in the implicit method time propagation, spatial step size δx (and δy in 2D), as well as the number of iterations N_{it} are defined as global constants. Also the lenghts of the domain in x and y directions, L_x and L_y, need be defined. In 2D calculations, adaptive grid refinement is usually needed to make the computation faster, and the resolution is multiplied with some factor M several times during the simulations. This means that δx, δy and δt are divided by M and the iteration numbers when doing that are defined in an array with name `'Refinepoints'`. 2D grid refinement is done with bicubic interpolation.

In the 2D version, there is also a Python script named `'plot.py'` for plotting the square modulus

of resulting wave function, $|\psi(x,y)|^2$, and potential energy $V(x,y)$, which are produced as output files. The names of the data files, number of spatial grid points and domain lengths have to be correctly defined in the 'plot.py' source file if they are changed from previous values. The xy coordinate system is defined so that $-L_x/2 \leq x \leq L_x/2$ and $-L_y/2 \leq y \leq L_y/2$.

3 Examples

The examples demonstrate how to use the program to find a high excited state with many nodes for an anharmonic potential well $V(x) \propto x^4$, for a 2D rectangular potential well and for a 2D supercircle shaped potantial well with finite potential step at the rectangular or supercircular boundary. Units with $\hbar = m = 1$, where $m\hat{\text{A}}$ is the particle mass, are used in all examples.

3.1 Excited state of quartic 1D potential well

In this 1D example, the system is a 1D anharmonic potential well with units $\hbar = m = 1$. The potential energy is

$$V(x) = 0.25x^4. \tag{6}$$

The simulation had 400 iterations with time interval of about $T = 0.25$ on each iteration. The target energy was $E_t = 12.5$, which is close to the value $E_8 = 12.738$ calculated with the shooting method for 7th excited state of this system. An optimal value of T for convergence should be close to $T = \frac{\pi}{E}$, where E is the energy of the eigenstate that is sought as a result. The spatial domain had length $L = 20$ and there were 1200 grid points. The time step was $\delta t = 0.01$. The resolution (in either space or time stepping) was not refined at any point in the calculation, because in 1D the initial values of δt and δx can be made small enough for good accuracy without making the process too slow. The initial wave function was a multiple of a sine function and a Gaussian.

The energy seemed to converge to about $E = 12.733$, which is close to the shooting method result. Squared modulus wave function $|\psi(x)|^2$ is shown in Figure 1, and it clearly has 7 nodes as supposed for the 7th excited state of a 1D system.

The source code prints both the energy convergence and the squared wave function values to standard output, and the latter needs to be transferred to a separate text file to be plotted with Grace or other similar application.

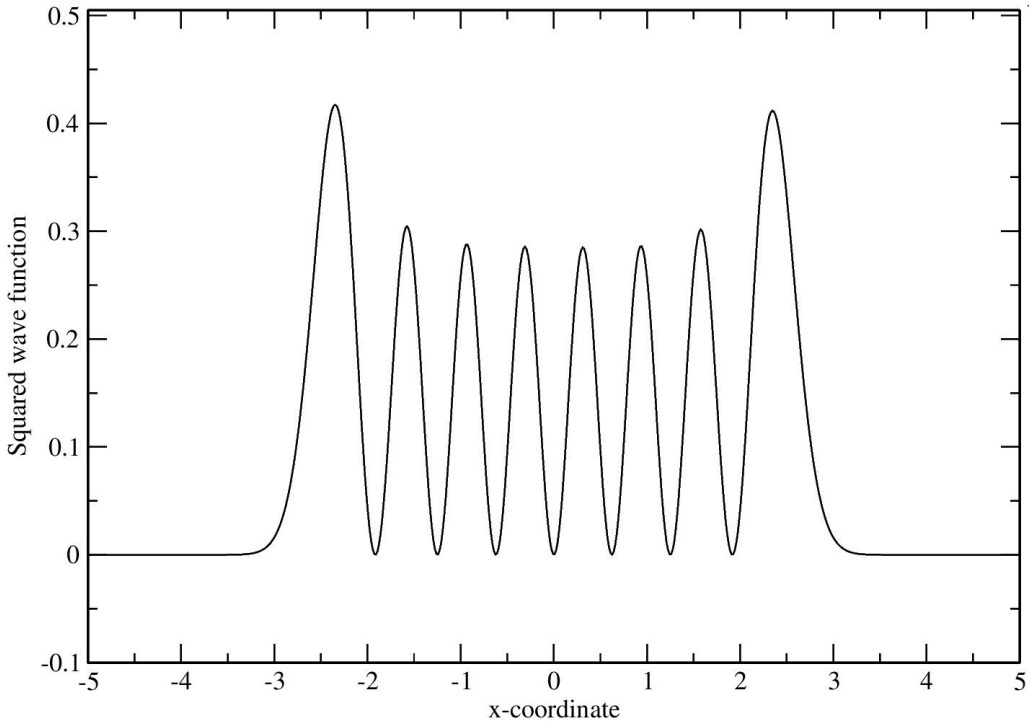

Fig. 1: The absolute square wave function $|psi(x)|^2$ computed for a 1D potential well with $V(x) = \frac{1}{4}x^4$.

3.2 Rectangular 2D finite potential well

In this example, the $V(x)$ is 0 inside a rectangle of length 1.3 in the x-direction and length 1 in the y-direction. The reason for choosing different side lengths was to avoid complications from having subspaces of degenerate eigenstates with same energy eigenvalue. The potential step at the boundary of the rectangle is $V_0 = 2 \times 10^5$ to have a result close to that of a hard-walled 2D box ($V_0 \to \infty$). The trial energy was $E_t = 46.0$ to attempt to converge towards the eigenstate of $\hat{H}$ equivalent to that of a hard-walled box with quantum numbers $n_x = 2$ and $n_y = 3$. In the $V_0 \to \infty$ case the exact energy eigenvalue of that state is about 46.05. The time length of one iteration was set to $T \approx 0.068$ and the number of iterations was $N_{it} = 1000$. Initially, the grid contains 100 points in both x and y directions and the time step is $\delta t = 0.004$. Resolution is increased 1.5-fold at iterations 800, 940, 980 and 992. The initial wave function is a sum of two Gaussian functions constructed to not be likely to be completely orthogonal with any eigenstate of $\hat{H}$.

The energy convergence is shown in the output file `'rectanglestdout.txt'` and the data files for plotting the wave function and potential energy with the Python script are named `'psi_2d_data.csv'` and `'potential_2d_data.csv'`.

In the result, the energy eigenvalue seems to converge to something near $E_{23} = 45.8$.

The $|\psi(x,y)|^2$ and $V(x,y)$ plots are shown in Figure 2. There it is apparent the the solution has two nodes in the x-direction and one node in the y-direction, corresponding to the state with quantum numbers $n_x = 3$ and $n_y = 2$.

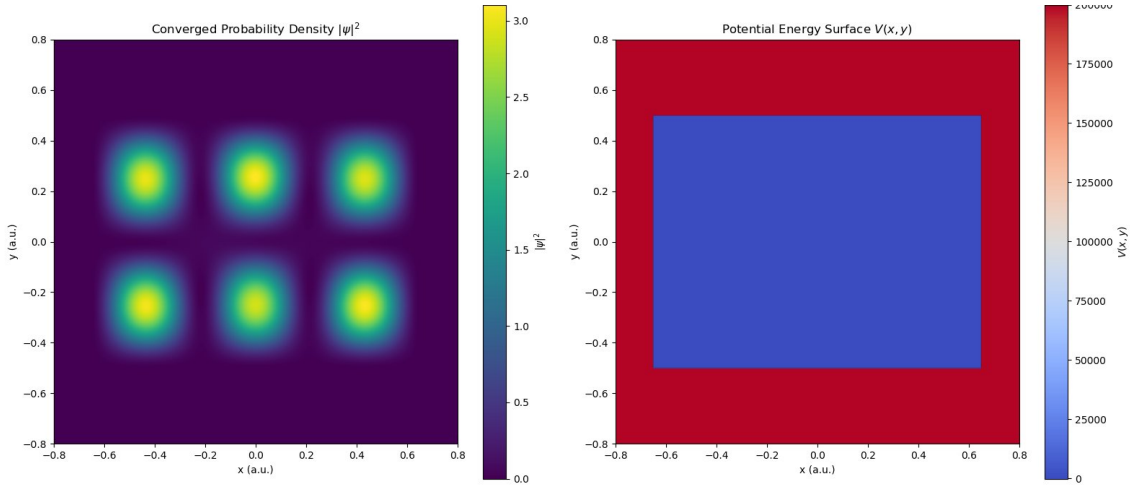

Fig. 2: 2D plots produced by the Python script from the results for an excited state of a rectangular potential well.

3.3 Supercircular 2D finite potential well

A supercircle is a 2D curve defined with the equation

$$|x|^q + |y|^q < r^q, \tag{7}$$

where r is something equivalent to the radius in the circular $q = 2$ case. The absolute values are needed because q is not necessarily an integer divisible by 2. When $2 < q < \infty$, this curve has a shape that is something between a circle $q = 2$ and a square $q \to \infty$.

In this example calculation, the potential energy $V(x,y)$ has value zero inside a supercircle with $q = 3$ and value 2×10^4 outside it. This is similar to the system in my publication [?] The radius parameter was set to $r = 1.063999$ to have a supercircle of area $A = 4.0$.

To find an approximation to the eigenstate of $\hat{H}$ corresponding to the second excited state of the circular $q = 2$ equivalent, the target energy was set to $E_t = 11.0$. The time interval T in each iteration has value 0.286. Tnitially there are 120 grid points in both x and y directions and the time step has lenght 0.02. The resolution is adaptively refined 1.5-fold three times during the calculation. The total number of iterations is 600. Initial wave function was again set to be a sum of two Gaussians.

The energy eigenvalue converges to something around $E = 10.98$, as seen in the standard output. The $|\psi(x,y)|^2$ and $V(x,y)$ plotted with the Python script are shown in Figure 3.

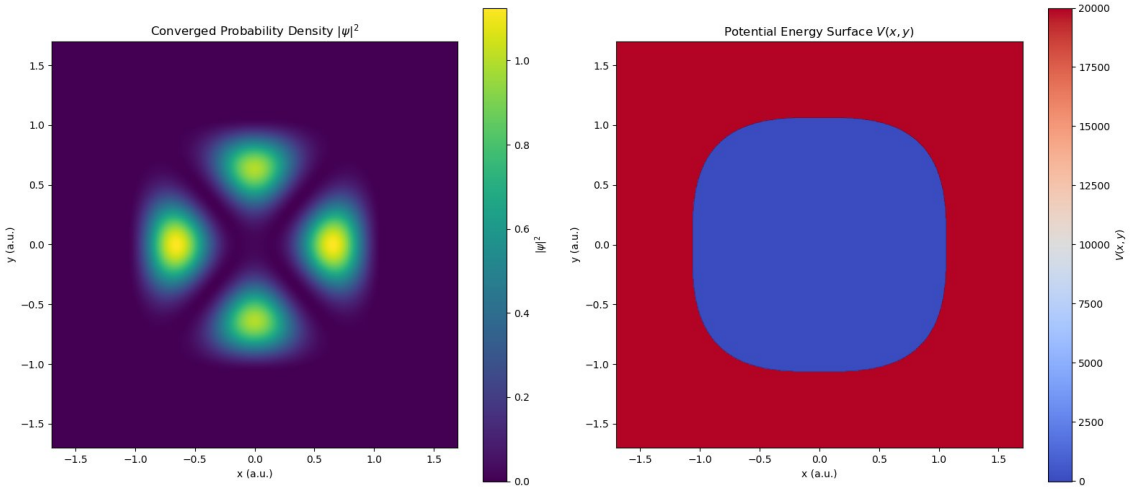

Fig. 3: A 2D plot of the approximate second excited state of particle in a supercircular potential well with shape parameter $q = 3$, area $A = 4$ and potential step of $V_0 = 20000$ at the boundary.

4 Additional comments

The time averaging used in my C++ code has some similarity to how a measurement makes a superposition of eigenstates collapse to one with a definite value of the measured observable. Any measurement process spans a nonzero time interval, and therefore also has something to do with a time average.

The calculation of excited states with this program is clearly faster if there is a good initial approximation for the wave function and energy value. When finding an approximation for an excited wave function with the usual sequential calculation using imaginary propagation and starting from the ground state, error accumulates while moving to higher energy states. The type of time-averaged state calculation as in this program can also be used for improving the accuracy of those results, without depending on the accuracy with which the lower energy eigenstates have been computed.

Using this method for systems of more degrees of freedom quickly becomes difficult when there are many position coordinates, and it's probably difficult to do this for anything more than a 2-dimensional helium atom (4 degs of freedom), even with supercomputing resources, as the linear systems in implicit method time propagation quickly contain very large matrices with increasing number of space coordinates. This situation may change if quantum computing allows for better scaling of computation time as a function of the number of spatial grid points.

References

[1] https://github.com/TeemuIsojarvi/meanstate (Retrieved 22.1.2026).

[2] W. H. Press, S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, *Numerical Recipes: The Art of Scientific Computing 3rd Ed.* (Cambridge University Press, 2007).

[3] T. Isojärvi, *Quantum mechanics of particles trapped in a Lamé circle or Lamé sphere shaped potential well*, Rev. Mex. Fis. **67 (2) 206-218.**