Jacobi Method Solution of Two-Electron Problem with External Harmonic Potential

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Abstract

Numerical methods are utilized to compute energy levels of a one- and two-body Schrodinger equation system in a central potential. Through this computation we are able to validate the Jacobi method of solving the eigensystem in a compact way with analytic solutions for comparison. Extending the traditional Jacobi method, a slightly modified "cyclical" Jacobi method is also utilized and is found to improve performance.

Contents

1 Introduction

Simple quantum mechanical systems have long been modelled by a harmonic oscillator potential in the Schrodinger equation due to the generally harmonic properties of central potentials. This is an advantageous approximation due to the availability of exact, analytic solutions while still applying to a wide range of near-equilibrium systems. For these reasons the simple quantum harmonic oscillator system is an excellent test case for implementing simple eigensystem solvers such as Jacobi's method. In this work, we test Jacobi's method as applied to the one-electron and two-electron quantum harmonic oscillator system to resolve the eigenvalues and eigenvectors which correspond to energy levels and wavefunctions respectively. Due to the flexibility of the harmonic oscillator model, we also investigate the effect of varying potential strength and how the Jacobi algorithm responds.

In addition to the emphasis on the Jacobi method in terms of the physical problem we apply it to, we also investigate multiple variants of the algorithm itself. As it is detailed in the following sections, we will compare the classical Jacobi method with a more modern variant known as the 'cyclical' Jacobi method. This cyclical variant better utilizes the power of modern computers, which of course were not available at the time Jacobi formulated his method. The extent of the improvements will be determined and compared to here.

2 Theory

The radial Schrodinger equation for a single electron in a spherically-symmetric central potential can be written as

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{l(l+1)}{r^2}\right)R(r) + V(r)R(r) = ER(r) \quad (1)$$

with $R(r)$ being the radial wave function of the electron and $V(r)$ as the central potential, which we choose to be that of a harmonic oscillator,

$$V(r) = \frac{1}{2}m\omega^2 r^2, \quad (2)$$

from this setup we then the energies are known to be (using standard quantum number notation for n and l),

$$E_{nl} = \hbar\omega\left(2n + l + \frac{3}{2}\right) \quad (3)$$

Using the substitution, $R(r) = (1/r)u(r)$ and assuming no angular momentum we can rewrite our system as

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u(r) + \frac{1}{2}m\omega^2 r^2 u(r) = Eu(r)$$

Now further simplifying by using dimensionless variables dependent on an arbitrary parameter α and $\rho = r/\alpha$ gives,

$$-\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{d\rho^2}u(\rho) + \frac{1}{2}m\omega^2\alpha^2\rho^2 u(\rho) = Eu(\rho).$$

rearranging this,

$$-\frac{d^2u}{d\rho^2} + \frac{m^2\omega^2\alpha^4}{\hbar^2}\rho^2 u(\rho) = \frac{2m\alpha^2}{\hbar^2}Eu(\rho)$$

now a compact form can be written using the definitions $\alpha = \sqrt{\hbar/m\omega}$ and $\lambda = 2E/\hbar\omega$, which finally gives

$$-\frac{d^2u}{d\rho^2} + \rho^2 u(\rho) = \lambda u(\rho). \tag{4}$$

Extending this methodology to a two-body problem requires only a modification of the potential, $V(\rho) = \rho^2$ to the two-electron case [1]

$$V(\rho) = \omega_r^2\rho^2 + 1/\rho \tag{5}$$

To illustrate generality we now rewrite our PDE to apply to both orders of interaction,

$$-\frac{d^2u}{d\rho^2} + V(\rho)u(\rho) = \lambda u(\rho) \tag{6}$$

Numerical discretization can then be utilized in the same manner as our previous work [2] on account of a shared elliptical differential operator between the two i.e second-order diffusion-like behavior. For N grid points, dirichlet boundary conditions and a grid spacing h, the finite-difference stencil can be written as,

$$-\frac{u_{i+1} - 2u_i + u_{i-1}}{h^2} + V_i u_i = \lambda_n u_i, \qquad i = 1, \ldots, N$$

Which can be rewritten in the familiar tridiagonal matrix form:

$$\begin{pmatrix} \frac{2}{h^2} + V_1 & -\frac{1}{h^2} & & & \\ -\frac{1}{h^2} & \frac{2}{h^2} + V_2 & -\frac{1}{h^2} & & \\ & -\frac{1}{h^2} & \ddots & \ddots & \\ & & \ddots & \ddots & -\frac{1}{h^2} \\ & & & -\frac{1}{h^2} & \frac{2}{h^2} + V_{N-1} \end{pmatrix} \tag{7}$$

where we solve an eigenvalue system to resolve our quantum states.

2.1 Jacobi eigenvalue method

For solution of the straightforward eigenvalue problem the harmonic oscillator yields, we employ the Jacobi method. The goal of the algorithm is to diagonalize our symmetric matrix A by means of successive similarity transformations that preserve orthogonality,

$$S^T A S S^T \mathbf{v} = \lambda S^T \mathbf{v}$$

where the similarity transform operator S is the standard orthogonal rotation matrix

$$\mathbf{S} = \begin{pmatrix} 1 & 0 & \dots & 0 & \dots & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 & \dots & 0 & \dots & 0 \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ 0 & 0 & \dots & \cos\theta & \dots & \sin\theta & \dots & 0 \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ 0 & 0 & \dots & -\sin\theta & \dots & \cos\theta & \dots & 0 \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ 0 & 0 & \dots & 0 & \dots & 0 & \dots & 1 \end{pmatrix}, \tag{8}$$

As for a more detailed mathematical overview of the algorithm, we refer the reader to [1] where it is discussed in full. The core methodology behind the workflow can be outlined as such

1. Choose an off-diagonal matrix component (how to make this choice will be discussed in the following section).
2. Compute the angle of rotation required to zero out this component as well as its symmetric pair
3. Apply the similarity transform using this angle to the original operator
4. Repeat this process for all non-zero off-diagonal elements until the matrix is diagonal within some tolerance criteria

Once the final diagonal matrix is constructed the eigenvalues are fully determined and can be sorted if desired. Eigenvectors also can be determined through the iterative process simply by applying the computed transformations to the matrix columns.

Previously, it was mentioned that off-diagonal matrix elements need to be chosen in the iterative scheme. Traditionally, this choice consisted of the largest off-diagonal matrix at each iteration and is known as the classical approach[3]. This is reasonable considering the lack of computers at the time Jacobi formulated the method. If performing the iterations by hand, choosing the max off-diagonal at every iteration can reduce the number of iterations required thus simplifying the task. On modern computers however, this choice presents a

Table 1: Single electron eigenvalues (eV) for varying ρ_{max} with a grid size of N=500. The known analytic values for the lowest three eigenvalues are $\lambda = 3, 7, 11$.

	$\rho = 1$	$\rho = 2$	$\rho = 4$	$\rho = 5$	$\rho = 8$	$\rho = 10$
λ_1	10.15	3.52	2.99	2.99	2.99	2.99
λ_2	39.79	11.16	7.03	6.99	6.99	6.99
λ_3	89.14	23.52	11.07	10.99	10.99	10.99

Table 2: Single electron calculation timings for both algorithms.

N	t^{cyclic}	t^{classic}	$N_{\text{iter}}^{\text{cyclic}}$	$N_{\text{iter}}^{\text{classic}}$
50	0.017	0.068	55	3383
100	0.119	0.395	122	13721
150	0.381	1.913	172	31311
200	0.861	5.907	211	55990
250	1.851	14.291	275	88033
300	3.339	29.356	331	127325
350	4.933	54.060	382	173589
400	8.046	92.149	437	226925
450	11.615	148.050	482	289144
500	12.576	225.007	537	356950

disadvantage for moderately sized matrices in that it requires a potentially expensive search routine at every iteration to locate the maximum off-diagonal component.

3 Results

3.1 Single electron

In all cases, there are many dimensionless parameters that can be tuned based on desired accuracy and efficiency. Choices for these parameters were always calibrated with respect to the known (analytic) energies. Only considering the three lowest energies (3,7 and 11 eV determined analytically) we can illustrate a suitable choice of parameters. For testing, a maximum grid size of 500 was tested and corresponding ρ_{max} was determined with ρ_{max} varying between 1 and 10.

It is clear according to Table.1 that $\rho_{max} = 5$ provides sufficent accuracy. To illustrate the Jacobi methods convergence, we assess the number of iterations required for convergence with increasing grid size for both cyclical and classical,

As expected, both methods converge at an approximately equivalent rate (quartic) however the cyclical approach requires significantly fewer iterations. This is likely due to the highly structured nature of our matrix problem. Exact

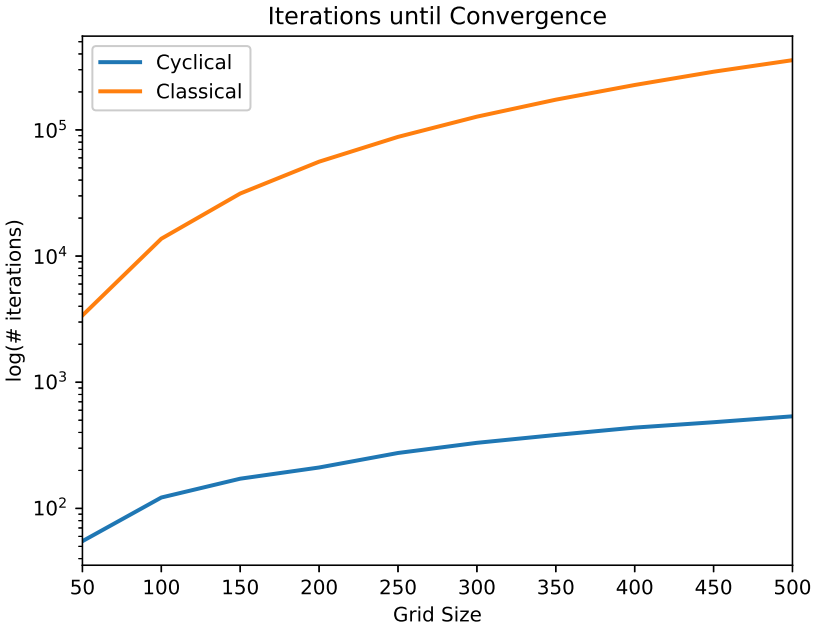

Figure 1: scaling of both cyclical and classical algorithms with respect to grid density for and $\rho = 5$.

Table 3: Energy eigenvalues of two-electron system for a grid size of N=500. The interaction strength is characterized by oscillator frequency, ω_r. Reference values are taken from [4].

	ω_r^{-1}	This Work	Ref. [4]
10	4	1.2504	1.2500
15	20	0.3500	0.3513
40	54.73	0.1644	0.1645

timings are shown in 2.

3.2 Two electrons

The extension to a two-electron problem introduces the potential parameter ω_r. Testing different values for this interaction strength is done in accordance with [4] where we have chosen several ρ_{max} values which converge each.

For the first three eigenvalues again, we present our results as well as that of [4] for comparison in Table.3. It is important to illustrate the physical significance of ρ and ω_r rather than solely their importance as convergence parameters in solving the eigenvalue problem. This is most easily visulized through the probability distribution of the ground state for a set of values shown in Fig.2. Larger values of ω_r correspond to a stronger interaction potential which will confine electrons to a more localized region about the classical electron distance. In more familiar terms, this would be analagous to the simple 1D potential well increasing in depth. The width of this potential well is analagously represented by ρ_{max} where the larger the value, the less localized the wavefunction. We observe this behavior by noting the rapidly increasing ρ values required to converge the solution when the interaction strength ω_r weakens. This is consistent with the oscillator model presented in [4] where we would expect high frequency oscillations to localize electrons.

Most importantly, this result validates our physical interpetation of the basic harmonic oscillator model for simple atomic systems. Higher frequencies ω_r lead to a stronger localization of electrons

4 Conclusions

For all tested cases the Jacobi method was highly accurate and straightforward to implement for multiple physical scenarios. There is significant speedup in modifying the algorithm to the cyclical variant but the overall convergence remains quartic. Although there are many modern specialized algorithms that may potentially perform more efficiently, Jacobis method remains accurate and overall fast for the tridiagonal quantum harmonic oscillator problem.

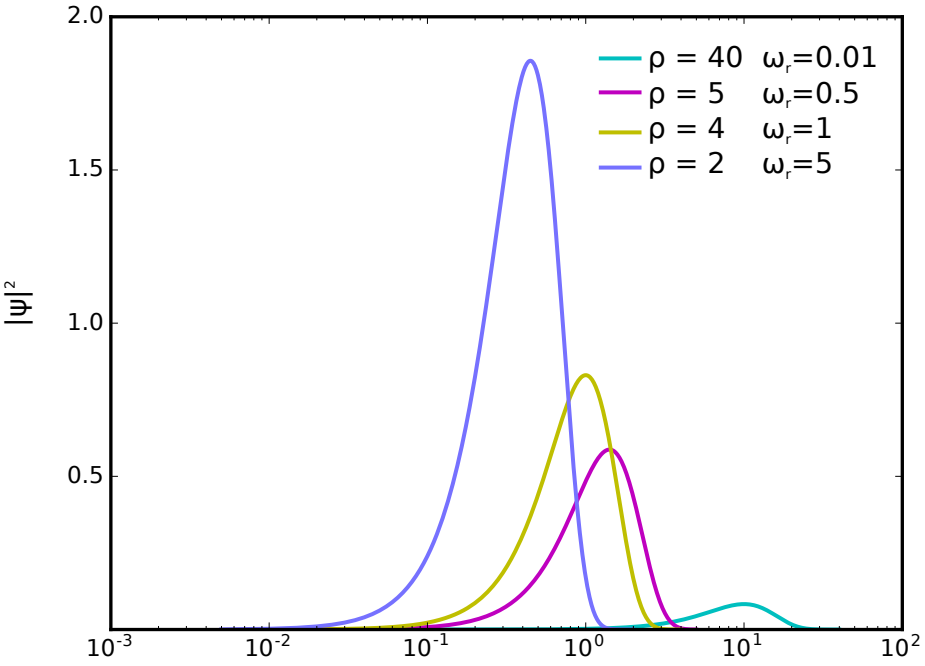

Figure 2: Ground state probability distributions for the two-electron harmonic oscillator model. Computed with a grid size of 500 and the cyclical jacobi method.

References

[1] M. Hjorth-Jensen. Lecture notes in computational physics, 2015.

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