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.

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

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

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,

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

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

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

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,

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

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

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

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,

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

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

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

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 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 eigenenergies [4]. Only considering the three lowest energies, a maximum grid size of 500 was tested and corresponding ρ_{max} was determined with $\rho_{max} = 5$ providing suffcient agreement. 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 timings are shown in 1.
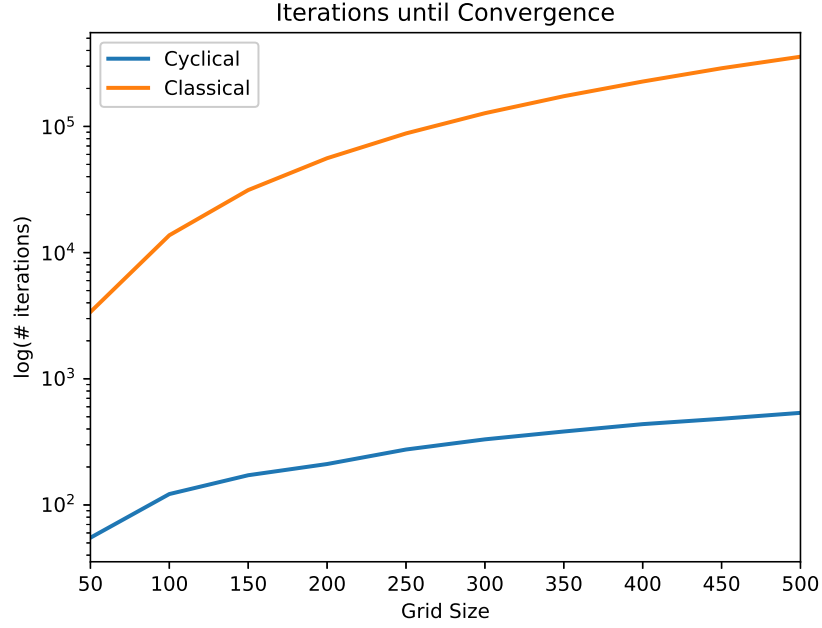
Figure 1: scaling of both cyclical and classical algorithms with respect to grid density for and $\rho = 5$.

Table 1: 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

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. The effect of the two-body interaction on the wavefunction is illustrated for the ground state probability distribution,
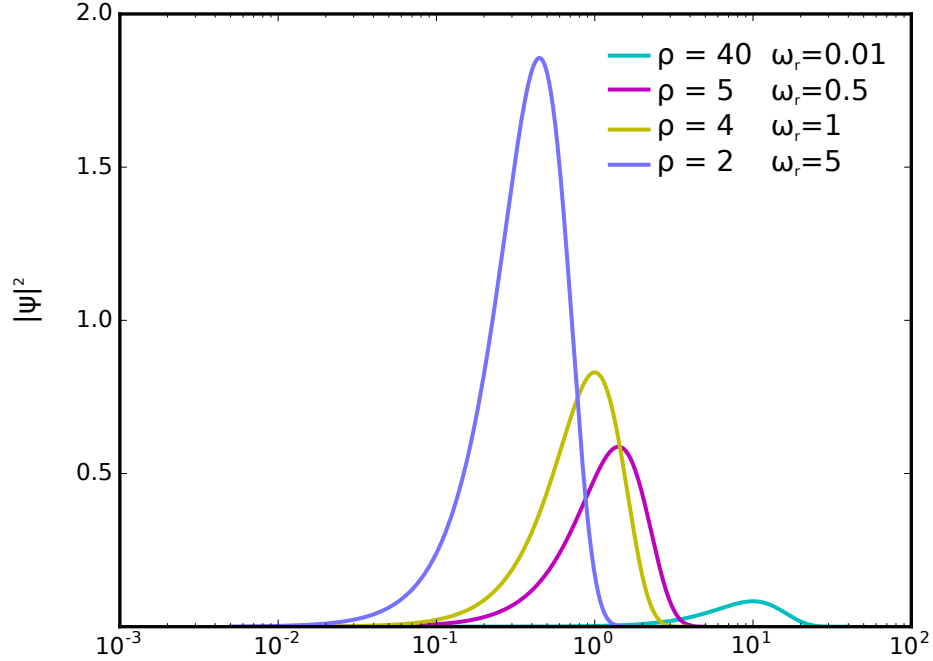

Figure 2: Ground state probability distributions for the two-electron harmonic oscillator model. Computed with a grid size of 500 and the cyclical jacobi method.

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.

References

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

[2] M. Santia. Phy905 project 1, 2017.

[3] William Press. *Numerical recipes in FORTRAN : the art of scientific computing.* Cambridge University Press, Cambridge England New York, NY, USA, 1992.

[4] M. Taut. Two electrons in an external oscillator potential: Particular analytic solutions of a coulomb correlation problem. *Phys. Rev. A*, 48:3561–3566, 1993.