Technical Information

Schroedinger.m: A Mathematica Package for Solving the Time-Independent Schrödinger Equation

John C. Hansen
Southwest State University, Marshall, MN 56258

Description of the Numerical Method

This package uses a discrete variable method (DVR) for solving the Schrödinger equation (*1, 2, 3*). In a DVR, a discrete set of points in position space, the *grid points*, forms the basis for a matrix representation of the Hamiltonian, which can then be diagonalized using usual methods. Such methods are built into Mathematica. An advantage of the grid representation over other matrix representations is that the eigenvectors are related to the familiar position-space wave functions in a simple manner. The elements of the eigenvectors are simply the values of the wave functions at the grid points.

To construct the Hamiltonian matrix in a grid basis, we write the Hamiltonian operator as a sum of kinetic and potential energy operators.

$$\hat{H} = \hat{T} + \hat{V} \tag{1}$$

In a position-space grid representation, the potential energy operator $\hat{V}$ is usually taken to be diagonal. The matrix elements are simply the values of the potential energy at the grid points. The kinetic energy matrix, however, is not diagonal. There are several possibilities for the representation of the kinetic energy operator on a grid, the most straightforward of which is a finite-difference formula for the second derivative (*4*). A representation that gives more accurate results is the so-called Fourier grid representation (*5, 6*). Using this method, the kinetic energy operator is first represented on a discrete grid in momentum space in which it is diagonal. A Fourier transform is then used to transform to the grid in position space. In practice, however, the Fourier transform does not need to be computed because a simple formula for the position space matrix elements can be derived. The derivation of this formula is given here.

We begin with a discrete set of eigenfunctions of the momentum operator, $\{|j\rangle, j = 0, \pm1, \pm2, \ldots\}$. For the convenience of normalizing these functions, they will be confined to a box in position space of length L with $-L/2 \le x \le L/2$, although later the value of L will be found to be immaterial. The x-space representation of these momentum eigenfunctions is

$$\langle x|j\rangle = L^{-1/2} e^{ik_j x}, \tag{2}$$

where $k_j = 2\pi j / L$. In practice, this basis will be confined to a finite set of N functions for which $|j| \le n$, where $N = 2n + 1$. Kinetic energy is represented in x-space by the operator

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \quad . \tag{3}$$

The matrix elements of this operator in the discrete momentum representation are found by applying the differential operator in (3) to the functions in equation (2), multiplying by $\langle i|x\rangle = L^{-1/2}e^{-ik_i x}$ and integrating over $[-L/2, L/2]$:

$$T_{ij} = \langle i|\hat{T}|j\rangle = \delta_{ij}\frac{\hbar^2 k_j^2}{2m} \tag{4}$$

An N-point discrete position representation may be defined in terms of the discrete position representation by choosing grid points $\{x_\alpha = \alpha L / N, \alpha = 0,1,\ldots,\pm n\}$ and applying the following transformation coefficients:

$$\langle \alpha | j \rangle = N^{-1/2} e^{ik_j x_\alpha} \tag{5}$$

This is a discrete Fourier transform and the DVR formed by the set of functions $\{|\alpha\rangle\}$ is called the Fourier-grid basis. In the Fourier grid basis, since it is essentially a position space representation, the potential energy is represented by a diagonal matrix with matrix elements equal to the values of the potential energy at the grid points (4).

$$\langle \alpha|\hat{V}|\beta\rangle = V_{\alpha\beta} = V(x_\alpha)\delta_{\alpha\beta} \tag{6}$$

The kinetic energy operator in this basis is found by applying the transformation in Equation 5 to the matrix elements in Equation 4.

$$\langle \alpha|\hat{T}|\beta\rangle = T_{\alpha\beta} = \sum_{j=-n}^{n} \langle \alpha|j\rangle T_{jj} \langle j|\beta\rangle \tag{7}$$

The result is

$$T_{\alpha\beta} = \frac{4\pi^2\hbar^2}{mN^3\Delta x^2}\sum_{j=1}^{n} j^2 \cos\left(\frac{2\pi(\alpha-\beta)j}{N}\right), \tag{8}$$

where $\Delta x = N / L$ represents the interval between adjacent grid points. This formula may be simplified considerably as we now demonstrate.

Suppose that the grid-based Hamiltonian matrix has been defined in terms of a value of L large enough so that it includes points for which the desired eigenfunctions are negligible. It is, as a matter of fact, necessary to do so for accurate results using any grid-based Hamiltonian. Then, for points at the extreme edges of the grid, where the wave functions vanish to a good approximation, it is obviously immaterial whether they are included. Under these circumstances, it should be permissible to formally define the kinetic energy matrix using Equation 8, with Δx fixed to the chosen interval size but with N much larger than the actual size of the matrix that is to be diagonalized. Thus, we may compute Equation 8 in the limit as n (and $N = 2n+1$) $\to \infty$ at constant Δx. Because the arguments of the cosine function in Equation 8 become more closely spaced as N is increased, the sum in this equation may be replaced by an integral giving

$$T_{\alpha\beta} \approx \frac{4\pi^2\hbar^2}{mN^3\Delta x^2}\int_0^n j^2 \cos\left(\frac{2\pi(\alpha-\beta)j}{N}\right)dj$$

$$\approx \frac{\hbar^2}{2\pi m\Delta x^2}\int_0^\pi y^2\cos[(\alpha-\beta)y]dy \qquad (9)$$

where the change of variable, $y = 2\pi j / N$, has been made, and the upper limit of integration replaced by π since $2\pi n / N = 2\pi n / (2n+1) \approx \pi$ for large n. Evaluating this integral, using the fact that $(\alpha-\beta)$ is an integer,

$$\int_0^\pi y^2\cos[(\alpha-\beta)y]dy = \frac{2\pi}{(\alpha-\beta)^2}(-1)^{\alpha-\beta} \quad \text{for} \quad \alpha \neq \beta \quad ,$$

$$\text{and } \frac{\pi^3}{3} \text{ for } \alpha = \beta. \qquad (10)$$

Substituting Equation (10) into Equation (9), we find

$$T_{\alpha\beta}\left(\frac{\hbar^2}{m\Delta x^2}\right)^{-1} = \frac{(-1)^{\alpha-\beta}}{(\alpha-\beta)^2} \quad \text{for } \alpha \neq \beta,$$

$$\text{and } \frac{\pi^2}{6} \text{ for } \alpha = \beta. \qquad (11)$$

The Mathematica package described in this paper constructs a grid of 30 equally spaced points in a range of x's specified by the user. The user may change this setting to construct a grid of greater or fewer points. In any case, the independent variables are the maximum and minimum values of x and the number of grid points in this range. The package includes definitions of the matrix elements of $\hat{T}$ from Equation 11 and $\hat{V}$ from Equation 6. In these expressions, the values of $\hbar$ and particle mass m are left unspecified. The user must supply numerical values for these, which effectively set the units for the problem. The user must also specify a potential energy function in one of several ways. Upon command, the package will construct the $\hat{T}$ and $\hat{V}$ matrixes, sum them to obtain the Hamiltonian, determine the eigenvectors and eigenvalues, and sort them. It also truncates the list of eigenvectors according to a user-specified energy range. It uses Mathematica's built-in routines for solving eigensystems. The eigenvectors are normalized so that

$$\sum_{\alpha=1}^{N}\psi_\alpha^*\psi_\alpha = 1 \ .$$

This is different from conventional normalization of position-space wave functions. It assures that these eigenvectors can be used to calculate matrix elements of operators using straightforward matrix multiplication of these eigenvectors with matrix representations of operators in the Fourier grid basis. For this purpose, matrix representations of several observables are defined in the package and available to the user.

The package also defines commands for interpolating between grid points to obtain continuous wave functions, which are normalized in the usual manner. The relation between the continuous and discrete eigenfunctions at the grid points is

$$\psi(x_\alpha) = \frac{\psi_\alpha}{\sqrt{\Delta x}} \quad .$$

Continuous solutions are appropriate whenever one wishes to examine the wave functions graphically or whenever an integral over part of the wave function's range is required. An example is calculating the probability of finding the particle in a particular region of space.

Citations

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