Computationally Calculating Expectation Values for the Time Independent Schrodinger Equation

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Introduction

The one-dimensional time-independent Schrodinger equation is as follows:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x) \tag{1}$$

The eigenfunctions and eigenvalues of the Hamiltonian $(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x))$ are the allowed wave functions and energies, respectively, for a given potential. After finding the allowed wave functions, one can calculate expectation values, which give the average value of an observable measured in many identically prepared systems. Suppose we have a set of ψ_n's corresponding to a particular potential. To calculate the expectation value of an observable o, one acts the operator corresponding to that expectation value on the n^{th} wave function, and takes the inner product of the n^{th} wave function with this quantity:

$$\langle o \rangle = \langle \psi_n | \hat{o} | \psi_n \rangle \tag{2}$$

Commonly calculated expectation values (for one-dimensional wave functions) include position (x), position squared (x^2), momentum (p), and momentum squared (p^2).

Any of the aforementioned expectation values can be calculated computationally by solving the TISE as a matrix eigenvalue problem to find a set of allowed wave functions, representing the eigenfunctions as a matrix, defining the requisite operator matrix, and writing the expectation value calculation as matrix multiplication. Suppose we have a set of eigenfunctions (ψ_n's) for a particular potential. We can represent this set of eigenfunctions in matrix form as

$$A = \begin{bmatrix} | & | & ... & | \\ \psi_1 & \psi_2 & ... & \psi_n \\ | & | & ... & | \\ ... & ... & ... & ... \end{bmatrix}$$

where each matrix element a_{mn} gives the m^{th} element of the n^{th} wave function. The operator corresponding to $\langle x \rangle$ multiplies ψ_n by x. Hence, the operator matrix for $\langle x \rangle$ must be diagonal, and can be written as:

$$\hat{x} = \begin{bmatrix} x & 0 & 0 & ... \\ 0 & x & 0 & ... \\ ... & ... & ... & ... \\ ... & 0 & 0 & x \end{bmatrix}$$

Multiplying the two matrices $\langle \hat{x} \rangle$ and A gives

$$\hat{x}A = \begin{bmatrix} x\psi_1 & 0 & ... & 0 \\ 0 & x\psi_2 & ... & 0 \\ ... & ... & ... & ... \\ ... & 0 & 0 & x\psi_n \end{bmatrix}$$

Taking the transpose conjugate of the matrix A to rewrite the eigenvector matrix in row form, and multiplying the matrix $\hat{x}A$ by this matrix from the left, results in a matrix with the expectation values of $\hat{x}$ for each ψ_n along the diagonal. Any non-diagonal elements in this matrix are the matrix elements for transitions between the $\psi_{m^{th}}$ and $\psi_{n^{th}}$ states. Non-zero diagonal elements show that a transition between the $\psi_{m^{th}}$ and $\psi_{n^{th}}$ states is non allowed.

To find $\langle x^2 \rangle$, the operator matrix is defined with x^2 along the diagonal, as opposed to x. The rest of the procedure is identical to that described above.