

This document describes:

- a partial differential equation (the quantum Hamiltonian) which is commonly used in physics and chemistry
- how to approximate this differential equation to find solutions using linear algebraic techniques
- two examples of both historical and computational interest

## Summary

The Hamiltonian operator  $H(\mathbf{x})$  on functions  $y(\mathbf{x})$  is a sum of Hermitian operators that has the form

$$H(\mathbf{x}) = c\nabla^2 + V(\mathbf{x})$$

where  $c$  is a constant,  $\nabla^2$  represents the Laplace operator and  $V(\mathbf{x})$  is a multiplicative term. We look for solutions to the eigenproblem

$$H(\mathbf{x})(y(\mathbf{x})) = c\nabla^2(y(\mathbf{x})) + V(\mathbf{x}) * y(\mathbf{x}) = \lambda y(\mathbf{x}).$$

This equation can have *bounded* solutions which have compact support over  $\mathbf{x}$  (i.e.,  $y(\mathbf{x}) = 0$  outside of finite boundaries for the  $\mathbf{x}$  variables) and/or *unbounded* solutions which do not have compact support, depending on the characteristics of the multiplicative  $V(\mathbf{x})$  term. (In the physics examples below,  $V(\mathbf{x})$  will be potential energy.)

For our application, we assume a single spatial dimension  $x$  and a  $V(x)$  which supports bounded solutions, and are interested in finding the bounded solution which has no nodes; that is, the function does not change sign within the boundaries. (This eigenvector of  $H$  is also the one with minimal eigenvalue.) We will be working with finite boundaries in space and will use a discretization that approximates the differential equation with a matrix equation. In one dimension, the Laplace operator on a function  $y$  becomes simply the second derivative of  $y$ , whose three-term approximation by a central difference is

$$\frac{d^2}{dx^2}y(x) \approx (\Delta x)^{-2} [y(x + \Delta x) - 2y(x) + y(x - \Delta x)]$$

On a discretized domain with  $N$  points

$$[-(N/2)\ell, (N/2)\ell]$$

this gives rise to a tridiagonal matrix

$$\begin{array}{cccccccc} & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ \dots & 0 & -1 & 2 & -1 & 0 & 0 & 0 & \dots \\ \dots & 0 & 0 & -1 & 2 & -1 & 0 & 0 & \dots \\ \dots & 0 & 0 & 0 & -1 & 2 & -1 & 0 & \dots \\ & & & & & & & & \end{array}$$

which when combined appropriately with the  $V(x)$  term generates a tridiagonal matrix  $M$  operating on  $y$ , for which we have a standard eigenvalue problem

$$My = \lambda y$$

Assuming that we have chosen our spatial bounds well and have a sufficiently fine discretization of space, the eigenvector of this matrix with minimal eigenvalue should give us a good approximation for the smoothly varying eigenfunction of the Hamiltonian.

## Physics Background

In quantum physics, the eigenvalues of the Hamiltonian represent energy, with the Laplace operator giving the energy of motion and the multiplicative  $V(x)$  term the potential energy. As such, the eigenvalues  $\lambda$  are generally renamed  $E$ . Further, the eigenvectors of the Hamiltonian are typically labeled by the Greek letter  $\psi$  and are

interpreted as probability amplitudes (that is,  $|\psi(x)|^2$  is a probability density function). The eigenvector problem is known as the time-independent Schrodinger equation

$$H(x)(\psi(x)) = E\psi(x),$$

where for a single spatial dimension

$$H(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

(in this expression,  $m$  refers to the mass of the system and the constant  $\hbar$  gives the proper units for energy). The solutions to this equation are often called wavefunctions, because there is a more general form (the time-dependent Schrodinger equation) which relates the Hamiltonian to a derivative with respect to time, in a form that is well-known to describe the behavior of waves. The solutions are also often referred to as *states*, and when physicists specify the state of a system they are usually referring to a particular eigenvector of the Hamiltonian or some linear combination of these eigenvectors.

The solutions of a Laplacian equation locally look like  $e^{ix\omega(x)}$ . The frequency  $\omega(x)$  is related to the difference  $E - V(x)$ ; when this value is positive,  $\omega(x)$  is real, but when it is negative  $\omega(x)$  is imaginary. Thus, where the energy is greater than the potential function the wavefunction is vaguely sinusoidal (and actually sinusoidal when  $V(x)$  is constant), but where the energy is less than the potential the wavefunction decays exponentially. (The solution where it increases exponentially cannot be a probability amplitude and is thus unphysical.)

### Bounding and Discretizing

We assume that the lowest energy state is physically localized (the technical term is that it is a *bound state*) and therefore that the wavefunction is zero beyond our chosen  $x_{min}$  and  $x_{max}$  endpoints. In effect, we modify our potential so that it becomes infinity outside of our bounds, which forces the wavefunction to zero; if we pick the bounds wisely, the values we wish to calculate will be unaffected by this change. (This change, however, does have a major impact on the unbound states, and should not be used in a calculation for determining their properties.)

To get a matrix form for the Schrodinger equation, we choose the endpoints and some unit of distance  $\ell$  such that  $N = (x_{max} - x_{min})/\ell$ , and solve for the function  $\psi(x)$  at the chosen points. The Laplacian operator is converted into an  $N \times N$  matrix by approximating the second derivative using the central difference formula, which for general  $f(x)$  is

$$f''(x) \approx \ell^{-2} [f(x+\ell) - 2f(x) + f(x-\ell)].$$

At the endpoints, we take advantage of our assumption that  $f(x) = 0$  beyond our boundaries to get

$$f''(x_{min}) \approx \ell^{-2} [f(x+\ell) - 2f(x)]$$

$$f''(x_{max}) \approx \ell^{-2} [-2f(x) + f(x-\ell)].$$

The matrix that results is tridiagonal Toeplitz:

$$M' = \frac{\hbar^2}{2m\ell^2} * \begin{bmatrix} 2 & -1 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & 0 & \dots & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & \dots & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & -1 & \dots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \dots & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & \dots & 0 & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & -1 & 2 \end{bmatrix}$$

Our discretized eigenvector  $\psi$  then satisfies

$$M' * \psi + V \odot \psi = E\psi$$

where the  $\odot$  operator represents element-wise multiplication. (We use the column-vector notation that is standard in chemistry and physics. Since  $M$  is symmetric, there is essentially no difference if you prefer row vectors.) To move fully to standard matrix notation, we instead write

$$M\psi = (M' + \text{diag}(V))\psi = E\psi$$

where  $\text{diag}(V)$  represents a diagonal matrix with the elements of  $V(x)$  on the diagonal. The resulting matrix  $M$  is tridiagonal but no longer Toeplitz, since every diagonal element can be different. It should still be highly compressible in LARC, as the  $N \times N$  matrix has at most  $N + 2$  distinct scalars and large all-zero off-diagonal blocks.

## Harmonic oscillator

There are several simple potentials that are reasonable starting points for our work. The harmonic oscillator

$$V_h(x) = \frac{1}{2}m\omega^2 x^2 - E_z$$

is one of the first potentials studied in quantum physics classes because of its simplicity. The solutions to the Schroedinger equation with this parabolic potential have equally-spaced energy levels

$$E_n = (2n + 1)\hbar\omega/2 - E_z$$

so the lowest energy is simply  $E_0 = \hbar\omega/2 - E_z$ . The eigenvector corresponding to this energy is

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^2}{2\hbar}}$$

(The harmonic oscillator has natural units for length and energy, which allow for much simpler expressions

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2}x^2 \quad E_n = n + 1/2 \quad \psi_0(x) = \pi^{-1/4} e^{-x^2/2}$$

We present the full exposition assuming we will move on to more interesting potentials.)

Since this potential is symmetric about  $x = 0$ , it makes sense for  $x_{\min} = -x_{\max}$ . We can determine the proper value of  $\ell$  by trial and error, but since we know the correct  $\psi_0$  we should choose it to make a fairly smooth representation of the function.

A drawback of the harmonic oscillator is that there are an infinite number of bound states with increasing energy levels. However, the  $N \times N$  discretized version has only  $N$  eigenvalues; if we discretize using a large number of points  $N$ , the largest eigenvalue is (poorly) approximated by  $E_N$ . If we choose  $E_z$  to be  $E_N$  or larger, we will make  $E_0$  the eigenvalue with the largest norm value (it is of course negative), allowing us to try solving the equation using the power method.

## Morse potential

The Morse potential is another standard potential energy function. It is a three-parameter approximation for the potential of a diatomic molecule, and has both bound states and unbound states. (This would be true for any molecule, such as  $O_2$ ; if you add sufficient energy to the molecule it will dissociate and become unbound.) It has the form

$$V(r; D_e, r_e, a) = D_e \left(1 - e^{-a(r-r_e)}\right)^2 - D_e = D_e \left(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}\right)$$

which has its zero of energy at  $r = \infty$  and its minimum energy  $-D_e$  at  $r = r_e$ . The bound state solutions to this Schroedinger equation are complicated functions depending on generalized Laguerre polynomials; the the Wikipedia page “Morse potential” gives details. (There is also a nice graph comparing the Morse potential to the

harmonic oscillator potential.) These bound states are labeled from 0 to  $k = \lfloor \lambda - 1/2 \rfloor$  (with  $\lambda = \sqrt{2mD_e}/a\hbar$ ), and the eigenvalues for these  $k + 1$  states are given by

$$E_n = -\frac{\hbar^2 a^2}{2m} \left( \lambda - n - \frac{1}{2} \right)^2.$$

Our approach here is similar to that for the harmonic oscillator. We choose  $r_{max}$  to be sufficiently large, and  $r_{min}$  to be sufficiently small, that we would expect the wavefunction to be nearly zero at those points. (In a real diatomic potential  $V(0) = \infty$ . The Morse potential does not have that property, and it is possible to choose physically unrealistic parameters that would make the potential fairly small at  $r = 0$ .)

This function also has an infinite number of unbound states with  $E > 0$ , but simple matrix methods like that described above are not capable of solving for them. Our discretized matrix will enforce boundary conditions  $\psi(r_{min} - \ell) = \psi(r_{max} + \ell) = 0$ , effectively setting the potential to infinity at those points. This will have little effect on the bound states (assuming we have chosen our boundaries wisely) but forces the continuum of unbound states to be discretized. As a result, if we were to find the eigenvalues and eigenvectors of  $M$  for what are supposed to be unbounded states, the vectors found may have little resemblance to the correct eigenfunctions for the eigenenergies we see.