Project 2: Numerical Solutions to Schrodinger Equation in Plane Wave Basis

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(Dated: May 14, 2017)

We seek to create a python solver that can be used to solve the one-dimensional Schrodinger equation in the plane wave basis. While we typically solve the Schrodinger equation in position space, there are a few problems for which it is more convenient to solve in momentum space. One example is problems that feature periodic potentials. In this paper we will examine a particular periodic potential and solve the Schrodinger equation in the plane wave basis. We will convert back to position space to present plots of the wavefunctions.

I.   INTRODUCTION

The Schrodinger equation is perhaps the most important equation in all of quantum mechanics. It has been extensively supported by experimental data. The general form of the Schrodinger equation is as follows:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \tag{1}$$

However, most of the time we prefer to look at what are called stationary states. Essentially, we just ignore the time dependence of the Schrodinger equation–knowing that we can add it back later if we want. In that case we can write what is called the time independent Schrodinger equation as follows:

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

In this case we are interested in a particular periodic potential. We will take advantage of the plane-wave basis to more easily solve the Schrodinger equation for a periodic potential. Our potential of interest is this:

$$V(x) = 8\cos(50x) \tag{3}$$

II.   BACKGROUND

The qualitative behavior electrons in a solid arises due to the fact that the potential of solids is periodic. The signature characteristic of a periodic potential is the formation of energy bands. (Griffiths). A periodic potential models the potential founds in the crystals of solids. A periodic potential is defined as a potential that repeats after some distance:

$$V(x + a) = V(x) \tag{4}$$

Bloch's Theorem states that solutions to the Schrodinger equation for a periodic potential takes the form of
and satisfy the condition:

$$\psi(x + a) = e^{iKa}\psi(x) \tag{5}$$

This can be proved by use of the translation operator

$$Tf(x) = f(x + a) \tag{6}$$

For a periodic potential, the translation operator will commute with the Hamiltonian:

$$\left[\hat{T}, \hat{H}\right] = 0 \tag{7}$$

Because the translation operator commutes with the Hamiltonian the eigenfunctions of the Hamiltonian are simultaneous eigenfunctions of the translator operator. Thus,

$$T\psi = \lambda\psi \tag{8}$$

$$T\psi(x) = \psi(x + a) = \lambda\psi(x) \tag{9}$$

The eigenvalue of this eigen equation can be expressed as an exponential for some value of k

$$\lambda = e^{iKa} \tag{10}$$

Then eigenvalue equation becomes:

$$\lambda = T\psi(x) = \psi(x) = e^{iKa}\psi(x) \tag{11}$$

This is the first form of Bloch's theorem. It states that solutions to the Schrodinger in a periodic well are chosen so that the Hamiltonian of the eigenfunctions/wave functions there exists a vector k called the wave vector so that the translated wave function only differs by a phase factor (Morrison).

It turns out that the Fourier transform will be very important to us in this problem. We use the Fourier and inverse Fourier transforms to switch between position and momentum space. We will show how we do this in more detail later, but for now we will show the general form of the Fourier transform (in this case it shows a switch between the time and frequency domain–which is analogous to our switch between position and momentum space).

$$H(f) = \int_{-\infty}^{\infty} h(t) e^{2\pi i f t} dt \tag{12}$$

$$h(t) = \int_{-\infty}^{\infty} H(f) e^{-2\pi i f t} df \tag{13}$$

III. METHODS

The computation of electrons in a periodic potential The computation of the electronic energy structure of solids is not a simple problem and computational techniques must be employed. The central equation in the Schrodinger picture of quantum mechanics is the Schrodinger equation:

$$\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{r})\Psi = -i\hbar\frac{\partial\Psi}{\partial t} \tag{14}$$

the solutions to the Schrodinger equation are called the wave function. The wave functions being eigenvectors, its is realized that the wave function eigenvectors can be expressed in different basis sets.

$$\psi(x) = \sum c_i b_i(x) \tag{15}$$

where the coefficients are given by:

$$c_i = \int_{-a/2}^{a/2} b_i^*(x)\,\psi(x)\,dx = \langle b_i|\psi\rangle \tag{16}$$

Wave functions can be expressed in the delta function basis set or the plane wave basis set. The plane wave basis set is commonly used in the computation of wave functions and energies for periodic potentials. We define the plane wave basis set as follows:

$$b_i(x) = \frac{1}{\sqrt{a}} e^{ik_i x} \tag{17}$$

$$k_i = \frac{2\pi}{a} i \tag{18}$$

$$i = 0, \pm 1, \pm 2, ..., \pm N \tag{19}$$

The plane wave basis set is very similar to the mathematics of Fourier analysis. The Fourier transforms for switching between momentum and position space are defined as:

$$\tilde{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx$$

$$\Updownarrow$$

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(k) e^{ikx} dk$$

If the function is defined on a finite interval than the transforms change to:

$$f(x) = \frac{1}{\sqrt{a}} \sum_n \tilde{f}(x) e^{ik_n x}$$

$$f(k_n) = \frac{1}{\sqrt{a}} \int_{-a/2}^{a/2} f(x) e^{-ik_n x} dx$$

Because of the nature of Bloch wave functions we can take advantage of the the finite interval Fourier transform. Our function is periodic so we only have to worry about the behavior of one period. We can then extrapolate that behavior in either direction to create an infinite periodic potential.

As usual, to solve the Schrodinger equation as a matrix equation we need to build a Hamiltonian matrix. In this case, the elements of that matrix are:

$$H_{ij} = \langle b_i | H | b_j \rangle = \left\langle b_i | \frac{p^2}{2m} + V(x) | b_j \right\rangle \tag{20}$$

We can see that the kinetic term is diagonal and gives the following result:

$$\left\langle b_i | \frac{p^2}{2m} | b_j \right\rangle = \delta_{ij} \frac{\hbar^2 k_i^2}{2m} \tag{21}$$

Interestingly, it turns out that the potential term ends up being a Fourier transform. This is why the Fourier transform is so valuable in solving this problem. This is shown here:

$$\langle b_i|V(x)|b_j\rangle = \frac{1}{a}\int_{-a/2}^{a/2} V(x)e^{-i(k_i-k_j)x}dx = \frac{1}{\sqrt{a}}\widetilde{V}(k_i - k_j) \tag{22}$$

In order to to take the Fourier transform of our potential, we wrote our own discrete Fourier transform functions following *Numerical Recipes*. These equation show what we used to write our function, where h_k is the value of our potential at the point t_k.

$$h_k \equiv h(t_k), \quad t_k \equiv k\Delta, \quad k = 0, 1, 2, \ldots, N-1 \tag{23}$$

$$f_n \equiv \frac{n}{N\Delta}, \quad n = -\frac{N}{2}, \ldots, \frac{N}{2} \tag{24}$$

$$H(f_n) = \int_{-\infty}^{\infty} h(t)e^{2\pi if_nt}dt \approx \sum_{k=0}^{N-1} h_k e^{2\pi if_nt_k}\Delta = \Delta \sum_{k=0}^{N-1} h_k e^{2\pi ikn/N} \tag{25}$$

$$H_n = \sum_{k=0}^{N-1} h_k e^{2\pi ikn/N} \tag{26}$$

After completing our discrete Fourier transform we simply need to multiply by our step size to approximate a continuous Fourier transform.

$$H(f_n) \approx \Delta H_n \tag{27}$$

At this point we have our Hamiltonian matrix and all the methods from out previous project apply. We diagonalize the matrix to find eigenvalues and eigenvectors. Like last time our eigenvalues represent the energies of our eigenstates. But because we are working in momentum space our eigenvectors are representations of the wave function in momentum space. To get them back into position space we need to use the inverse Fourier transform. Once we have the wavefunctions back in position space we can do anything from last project like producing expectation values and plotting wavefunctions.

IV. VALIDATION

We validated our Fourier transform function by looking at the simplest possible cases: complex exponentials. When we did that we found that we returned arrays with all zeros
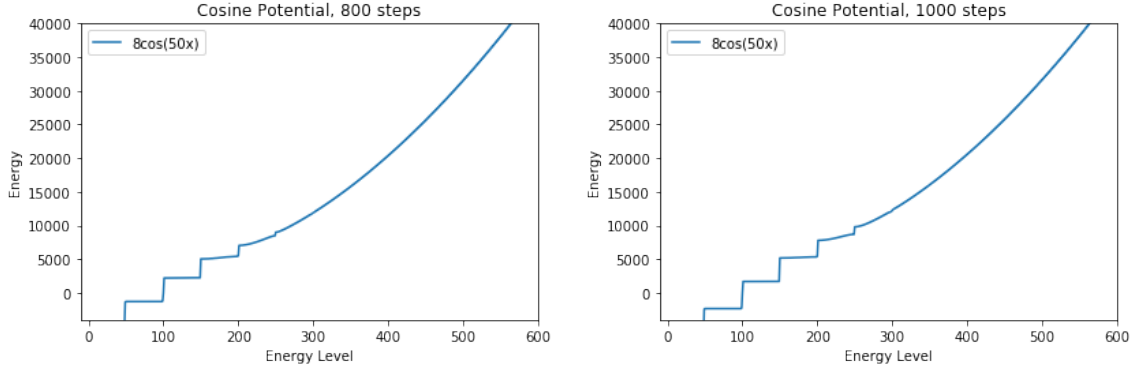
FIG. 1: This shows the eigen spectrum calculated for a differentm number of steps. It shows that as the number of steps changes—assuming it is high enought to account for how the potential changes—the spectrum does not change. This is a further form of validation.

and a single number, exactly what we expected. We also tested to ensure that our results were independent of the number of steps used. As shown below we found that was the case. These figures are shown at the end.

V.   RESULTS

We used the plane wave basis to solve for the eigenvectors and eigenvalues of the periodic potential given by:

$$V(x) = 8\cos(50x) \tag{28}$$

The wave functions for the periodic potential are shown in FIG. 2. The energy eigenvalue spectrum is shown in FIG. 3. The energy eigenvalue spectrum (the dispersion relation) illustrates the formation of band gaps. A band gap structure is the signature characteristic of a periodic potential. See the caption in FIG. 2 and FIG. 3 for a in depth physical explanation. Results are shown on the next page.

VI.   CONCLUSION

The Python program was successfully validated for this experiment. The sources of error in the experiment were: creating a finite matrix, using a number of steps that was computationally advantageous, and standard round off error from numerical computation.
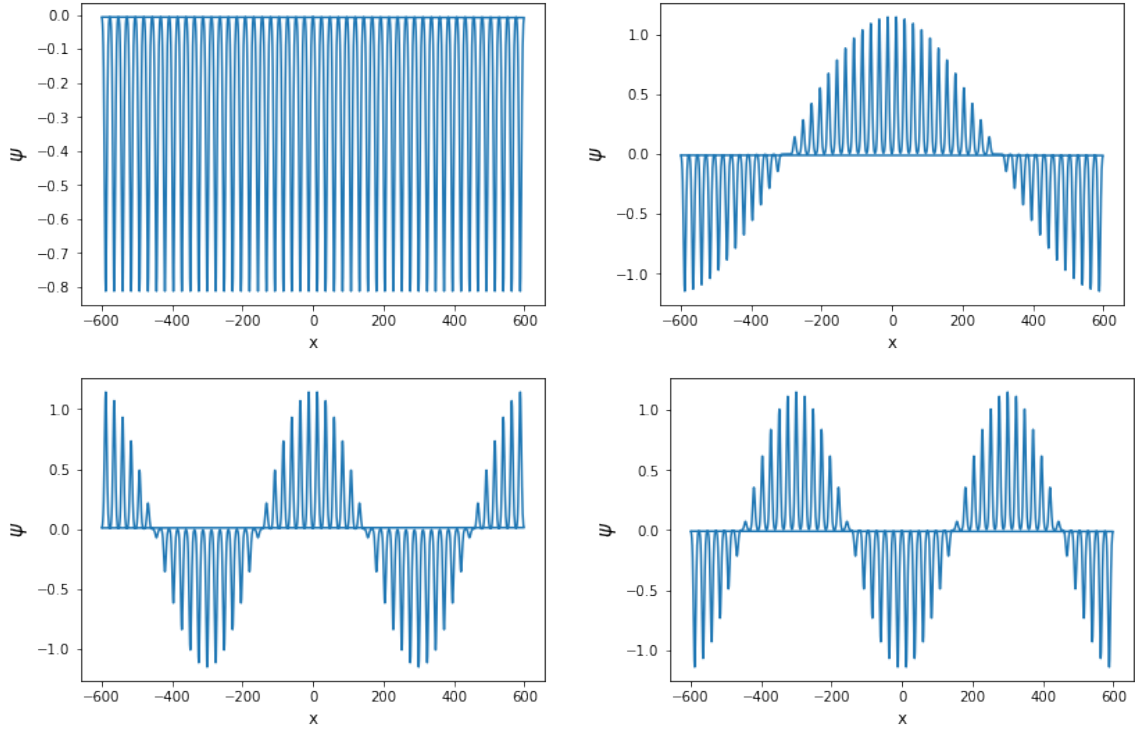
FIG. 2: These are the first couple of wave functions for a particle in a periodic potential. These wave functions are the Bloch waves of the potential and one can that the Bloch wave consists of the underlying wave-function that is modulated by the plane wave phase factor at the given k values.

We also had a lot of difficulty writing our discrete Fourier transform. It was difficult for us to reconcile the general form of the Fourier transform with the specific transform that we were trying to do in our problem. We validated our Fourier transform function by testing it on complex exponential. One thing that could be improved upon in further experimentation would be to take into account tunneling, the quantum mechanical process of particles moving through potential barriers. All in all though, we successfully observed the energy band structure of the periodic potential and the energy band structure is the most defining characteristic of a periodic potential that can be observed.

[1] Morrison, Estle, Lane, *Quantum States of Atoms, Molecules, and Solids*

[2] Griffiths David, *Introduction to Quantum Mechanics* (Second Edition, 2005).

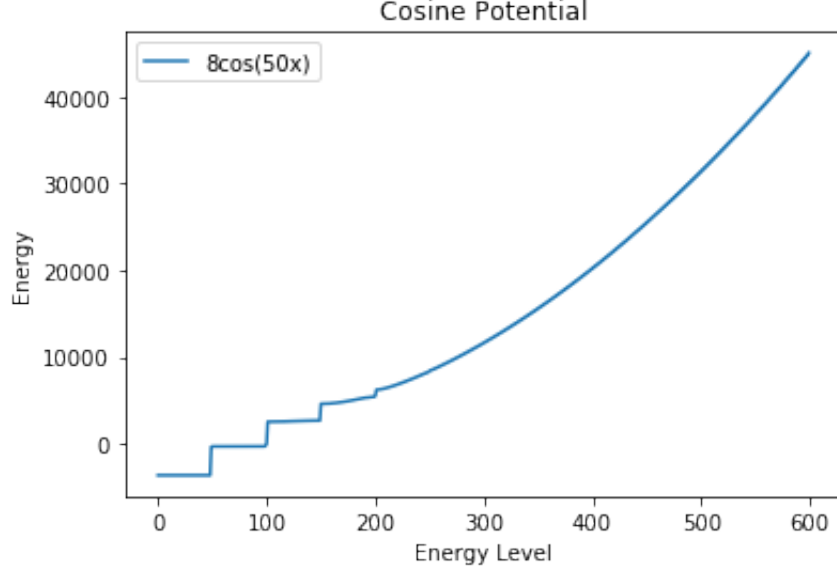[3] Giannozzi Paolo, *Numerical Methods in Quantum Mechanics*

FIG. 3: This figure represents a dispersion relation (energy versus energy level) for a periodic potential. The period potential being tested in this figure is the cosine potential we tested. A cosine potential is a simple model to represents a one dimensional atomic lattice because the electrons are more likely to be bound between the positive nuclei. A negative energy simply means that the electrons are bound. Positive energy means the electrons are essentially have higher energies than the bound states and are freely propagating through out the solid and are non localized to a deep atomic well. In this figure one can clearly see the bands and gaps in the dispersion relation around the 150 to 200 energy level. The straight lines in the plot represent the localized atomic states. The deep bound states are limited to energies very close bound states one would get for a single potential. This is why the slope of the dispersion relation is almost zero in the lower energy bound states because electrons can not take upon a wide range of energies in localized bound states. At higher energies one sees that the slope of the dispersion relation is more sloped and this represents a higher degree of energy freedom. These are the bands of the periodic potential. These band form at higher energies because the eigenfunctions become more dense and less localized in the high energy region of the potential ans the states approach the continuum well of the solid. The density of states increases the higher the energy of the particle is in the well and thus we see a more sloped dispersion relation corresponding to a band gap. Once the electron energies becomes higher then the potential well energy and reach energies up into the continuum energy region, the dispersion relation becomes continuous as that of a freely propagating electron.

[4] William H. Press, *Numerical Recipes*