The spectrum of the titled infinite potential well using numerical matrix methods

Wahaj Ayub and Rafi Ullah*

Department of Physics, School of Science and Engineering,

Lahore University of Management Sciences (LUMS), Lahore, Pakistan

Abstract

The infinite potential well forms one of the quintessential examples of one-dimensional systems taught in an introductory quantum mechanics course. The solution set is easy to derive and understand, and can explain many aspects of quantum theory. However, even small deviations from this problem, like a *tilted* well, an infinite well with a constant electric field, require the use of complex mathematical tools including Airy's functions. One way to address this however, is to use a matrix method to express the Hamiltonian in a basis. The eigenvalues and eigenfunctions can then be obtained numerically, where the only approximation is the finite number of basis states used. This approach gives students an intuitive understanding of more complex systems that cannot be solved analytically, as well as the use of matrix mechanics to solve problems beyond a two-level system. This work focuses on using this method to analyze the tilted potential well as well as find its optical spectrum. Since the potential is no longer symmetric, the position expectation value is no longer expected to be the center of the well. Counter-intuitive behaviour in the position expectations can shed some light on how the process of localization workks We also calculate transition dipole moments, which give us an insight into the selection rules as well as transition amplitudes for a tilted potential well.

* rafiullah@lums.edu.pk

I. INTRODUCTION

Given its straightforward analytical solution, it is no surprise that the infinite square well is one of the first examples given to many students of quantum mechanics [1]. The pedagogical value of this model system is clear, as it also has a straight forward interpretation in terms of a particle "trapped" in a box. Aside from this, the finite square well is also covered often, as this can demonstrate tunnelling phenomena. However, the solution for the finite square well is quite involved and involves the use of graphical solutions.

Another variation of the infinite well, the infinite tilted well remains missing from both pedagogical literature, as well as courses, despite some earlier work on solutions by Churchill and Arntz [2]. In Ref. [2], the Schrodinger equation is recast as Stokes equation, which admit Airy's functions as solutions. However, the normalization factors still have to be gleamed through graphical methods, keeping in mind the boundary conditions. A solution of this kind is overwhelming for most students coming into a quantum mechanics course. However, this kind of potential well has a direct relevance to heterojunctions of semi-conductors, where the potential can resemble a tilted well closely [3], as well as the potential for Bloch electrons at crystal boundaries [2].

In this paper, we propose a more coherent solution to the infinite tilted well, following the approach developed by Marsiglio [4]. Using this approach, it is easy to analyze any short range potential embedded in an infinite potential well. However, conveniently, our potential is already of this form. We see how this method can be implemented, discuss the resulting wavefunctions and present some interesting and potentially counter-intuitive observations. We aim to make this valuable as a pedagogical resource, that can be used to introduce students to how a matrix solution can be practically applied to a system for which an analytical solution is difficult.

II. APPROACH AND FORMALISM

As mentioned before, our approach is similar to the one developed by Frank Marsiglio in Ref. [4]. Here we present a quick review of the formalism for anyone unfamiliar with it.

The infinite square well potential is defined as

$$V_0(x) = \begin{cases} 0 & \text{if } 0 < x < a \\ \infty & \text{otherwise.} \end{cases} \tag{1}$$

The Hamiltonian is given by

$$\hat{H}_0 = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_0(x), \tag{2}$$

where m is the mass of the particle, and the eigenfunctions are

$$\phi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) & \text{for } 0 < x < a, \\ 0 & \text{otherwise.} \end{cases} \tag{3}$$

These eigenfunctions are orthonormal and complete, with eigenvalues

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \coloneqq n^2 E_1. \tag{4}$$

We introduce an arbitrary potential to the infinite potential well. This additional potential does not necessarily need to be a small perturbation. The new Hamiltonian will be given by

$$\hat{H} = \hat{H}_0 + V(\hat{x}). \tag{5}$$

We can then write the Schrödinger equation, in Dirac notation, as,

$$\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle. \tag{6}$$

Since the eigenstates of the unperturbed potential well are complete and orthonormal, we can write the state $|\psi\rangle$ as

$$\left|\psi\right\rangle = \sum_{n=1}^{\infty} c_n \left|\phi_n\right\rangle, \tag{7}$$

and

$$\hat{H}\left(\sum_{n=1}^{\infty} c_n \left|\phi_n\right\rangle\right) = E\left(\sum_{n=1}^{\infty} c_n \left|\phi_n\right\rangle\right) \tag{8}$$

This means that we can then write the Schrödinger equation in matrix form by taking an inner product with $\langle\phi_m|$

$$\left\langle\phi_m\right|\left(\sum_{n=1}^{\infty} \hat{H}\, c_n \left|\phi_n\right\rangle\right) = \left\langle\phi_m\right| E\left(\sum_{n=1}^{\infty} c_n \left|\phi_n\right\rangle\right), \tag{9}$$

which, by the linearity of the Hamiltonian and the inner product we can write as,

$$\sum_{n=1}^{\infty} \langle \phi_m | \, \hat{H} \, | \phi_n \rangle \, c_n = E \sum_{n=1}^{\infty} \langle \phi_m | \phi_n \rangle \, c_n = E c_m. \tag{10}$$

This can be written as

$$\sum_{n=1}^{\infty} H_{mn} c_n = E c_m, \tag{11}$$

where matrix elements of the Hamiltonian H_{mn} are

$$\begin{aligned} H_{mn} &:= \langle \phi_m \, | \, H \, | \, \phi_n \rangle = \langle \phi_m \, | \, H_0 + V \, | \, \phi_n \rangle \\ &= E_n \delta_{mn} + \frac{2}{a} \int_0^a \sin\left(\frac{m\pi x}{a}\right) V(x) \sin\left(\frac{n\pi x}{a}\right). \end{aligned} \tag{12}$$

So, any potential for which the integral in Equation (12) exists can be solved using this technique. We can populate the matrix by calculating the integral for different values of m and n. Now, we can use this formalism to solve the system to an arbitrary accuracy, as the method is exact except that we use a finite number of basis states $|\phi_n\rangle$. We can solve for the eigenvalues and eigenstates by diagonalizing the Hamiltonian matrix. We can denote the number of states used by the variable N.

III. THE TILTED POTENTIAL WELL

Now, we consider the example of the tilted potential well. We make use of Hartree atomic units ($e = \hbar = c = 1$). While the matrix elements can be evaluated numerically, it is possible for an undergraduate student to work out the resulting integrals analytically and this can be instructive. The additional potential $V(x)$, produced by applying an electric field to the particle, which is assumed to be an electron, is given by,

$$V(x) = -q\mathcal{E}_0 x, \tag{13}$$

where $\mathcal{E}_0$ is the magnitude of the electric field in atomic units, which we will call the tilt parameter and q is the charge of the particle. An electron has charge -1 in atomic units. So, our expression becomes

$$V(x) = \mathcal{E}_0 x. \tag{14}$$

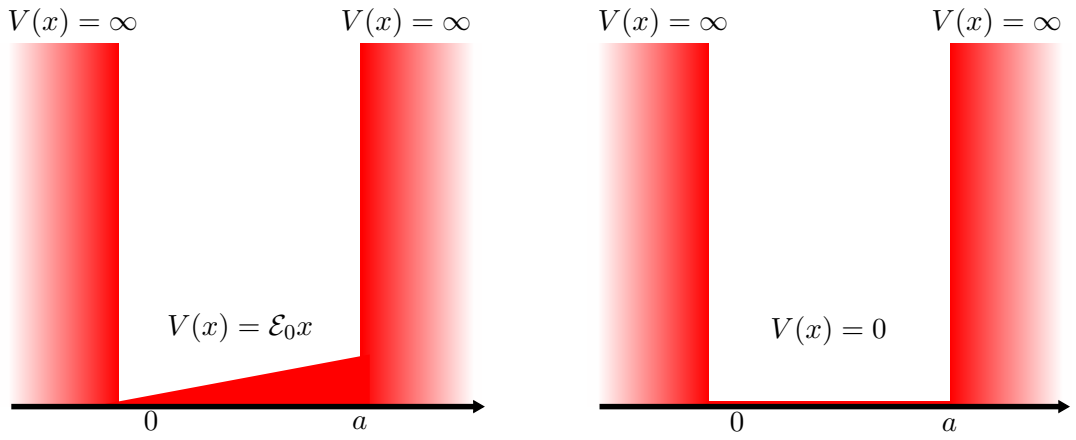


FIG. 1: The "Tilted" Potential Well, alongside the regular Infinite Potential Well

We want to calculate the matrix elements of $\hat{H}$:

$$H_{mn} = E_n\delta_{mn} + \langle\phi_n \,|\, V \,|\, \phi_m\rangle \tag{15}$$

$$= E_n\delta_{mn} + \mathcal{E}_0 \langle\phi_m \,|\, x \,|\, \phi_n\rangle \tag{16}$$

$$= E_n\delta_{mn} + \mathcal{E}_0 d_{mn}, \tag{17}$$

where

$$d_{mn} = \langle\phi_m|\hat{x}\,|\phi_n\rangle \tag{18}$$

is often called the transition dipole matrix element between states m and n. A detailed calculation of d_{mn} is present in Appendix A. However the result can be stated neatly as:

$$d_{mn} = \mathcal{E}_0 \left(\frac{a}{2}\right) \delta_{mn} + \left[\frac{-8a}{\pi^2}\left(\frac{mn}{(m^2-n^2)^2}\right)\right]_{m+n \text{ is odd}} \tag{19}$$

Using this, we write the matrix elements of the hamiltonian:

$$\langle\phi_m \,|\, H \,|\, \phi_n\rangle = \begin{cases} E_n + \mathcal{E}_0\left(\frac{a}{2}\right) & \text{if } m = n \\ \frac{-8a\mathcal{E}_0}{\pi^2}\left(\frac{mn}{(m^2-n^2)^2}\right) & \text{if } m+n \text{ odd} \\ 0 & \text{otherwise.} \end{cases} \tag{20}$$

From here, since we have obtained the Hamiltonian in matrix form, we can numerically diagonalize this matrix to obtain any desired information such as the eigenvalues and eigenvectors. Due to its simple theoretical framework this makes it a perfect way to introduce

undergraduates taking their first course to computational problem solving in Quantum Mechanics.

IV. COMPUTATIONAL DETAILS

The computations and plotting were done using a Jupyter Notebook with code written in Python. The code can be found on Github via a link in the bibliography [5]. This notebook has been made available in a format that would enable students to use it as a hands on exercise or tutorial.

We use the matrix elements of the Hamiltonian to produce an $N \times N$ matrix. Using numerical linear algebra tools from Python libraries, we find the eigenvalues and eigenvectors of the Hamiltonian, which correspond to our energy eigenvalues and eigenstates. The eigenvalues are calculated using the SciPy $linalg.eigh()$ function, which relies on LDL^T factorization. Thus we obtain our wavefunctions and energies, with the only approximation being the truncation of our basis set at N states. The resulting wavefunctions are plotted and shown in Fig. a.

The following parameters (all in atomic units) to simulate a titled well with a high tilt parameter:

$$\mathcal{E}_0 = 0.1\,\text{au},$$
$$a = 10\,\text{bohr},$$

where a is the length of the well. For the final results, a total of 200 basis states were used, though for this problem, as we will show, reliable results could be obtained using much fewer states. The idea of a basis and their usefulness remains unclear in popular textbook examples. Here we show the use of a basis and what role its size plays in numerical quantum mechanics. This is at the heart of quantum chemistry and condensed matter physics.

V. THE OPTICAL SPECTRUM

An important part of the behaviour of any quantum system is how it responds to external perturbations. We can study the probability that the system transitions from one state into another, given any specific perturbation. An important subset of this is optical transitions,

which are induced by propagating electromagnetic waves. To find the optical spectrum of the system we consider a linearly polarized electric field, that varies sinusoidally in time. We consider this as an additional potential $V(x,t) = E_0 x\cos(\omega t)$ in our system. According to Ref. Ref. [1], we can make use of the rotating wave approximation to get an accurate expression for the transition probability from state a to state b:

$$P_{a\to b}(t) = \frac{|V_{ab}|^2}{2\hbar^2\omega_r^2}\sin^2(\omega_r t)$$

where $V_{ab} = \langle\phi_a|V|\phi_b\rangle$, $\omega_r = \frac{1}{2}\sqrt{(\omega-\omega_0)^2 + \frac{|V_{ab}|^2}{\hbar^2}}$ and $\omega_0 = E_a - E_b$. It is easy to see that

$$V_{ab} = E_0\langle\phi_a|x|\phi_b\rangle = E_0 d_{ab},$$

and so the probability of transition is directly proportional to the square of the dipole matrix element. This also allows us to come up with selection rules and tell which transitions are "forbidden". A transition is forbidden if the corresponding matrix element is 0. We can reuse our result for d_{mn} to get

$$d_{mn} = \begin{cases} \frac{a}{2} & \text{if } m = n, \\ \frac{-8a}{\pi^2}\left(\frac{mn}{(m^2-n^2)^2}\right) & \text{if } m+n \text{ odd}, \\ 0 & \text{otherwise.} \end{cases}$$

We can then use to build up the transition matrix:

$$\frac{-8aE_0}{\pi^2}\begin{pmatrix} 0 & \frac{2}{3^2} & 0 & \frac{4}{15^2} & 0 & \dots \\ & 0 & \frac{6}{5^2} & 0 & \frac{10}{21^2} & \dots \\ & & 0 & \frac{12}{7^2} & 0 & \dots \\ & & & 0 & \frac{20}{9^2} & \ddots \end{pmatrix}$$

Note that we are only interested in the non diagonal elements of the matrix, and hence the diagonal elements have been set to zero to avoid clutter. The matrix gives us the dipole moments associated with our original system. We can also see that we have some selection rules: the transitions can only happen if $m+n$ is odd. We will see in later sections that the optical spectrum changes with the tilt parameter and these selection rules will no longer necessarily apply to the tilted potential well.

VI. RESULTS

A. Wavefunctions, Probability Densities and Energies

The wavefunctions and probability densitities for the first four states obtained through numerical diagonalization are plotted in comparison to the regular infinite potential well in Fig. 2.

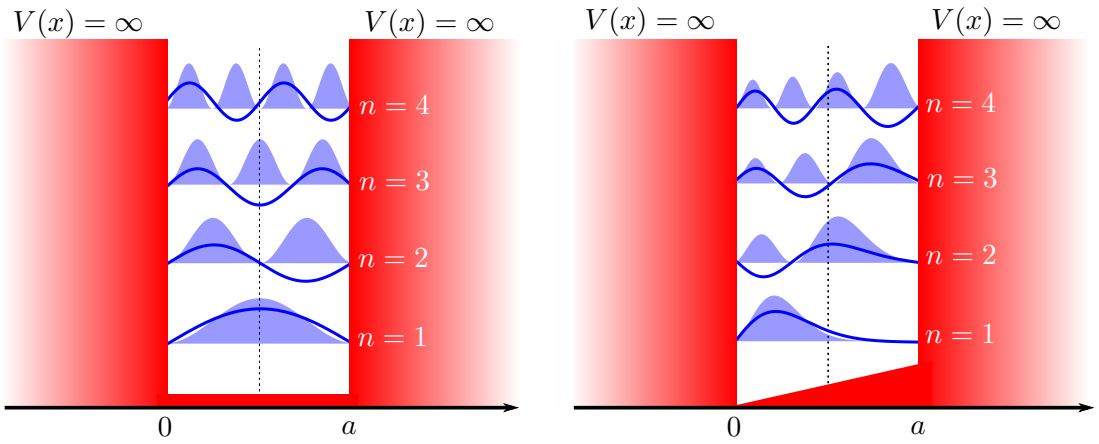


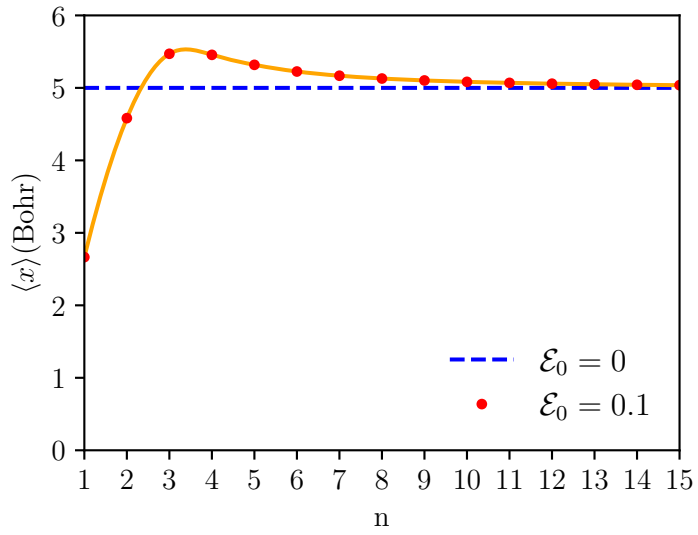
FIG. 2: The first four wavefunctions for the infinite potential well and tilted well

We see that the number of nodes for each wavefunction remains the same, but the probability densities are no longer symmetric around the center of the well. A larger number of nodes seems to bunch up in the left side of the well, however, the nodes on the right hand side are larger in size. This leads to interesting behaviour in the expectation value of position which we will further explore. Additionally, it is clear that the higher energy states are affected less by the presence of the potential.

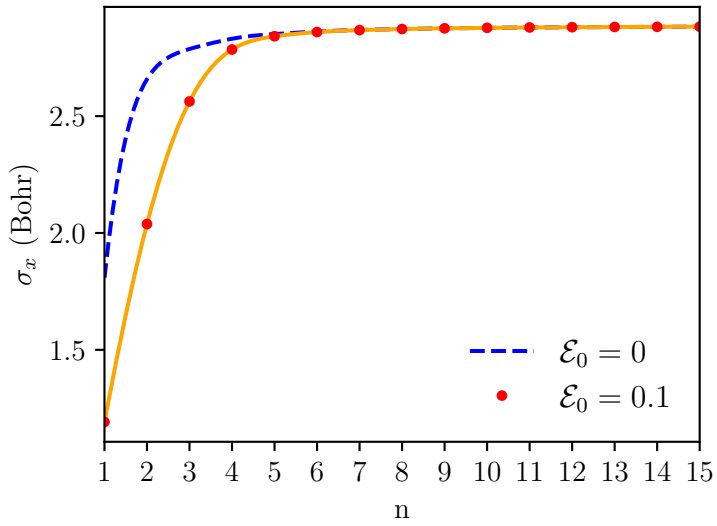
We also calculate average position of the electron in the well, which displays an interesting pattern. We can see this by plotting the position expectation values and uncertainties along the state n, as in Fig. 3.

We can see that the for the first states, the electron is pushed towards the left side of the well, with most probability of finding it in that half. However, curiously, the expectation values for later states, tend to favour the right side, despite the increased potential there. Fig. 4 presents a graphical summary of this observation.

The energy eigenvalues have been plotted in Fig. 5. We see that the energies follow a similar pattern to that of the regular infinite well, with most of the deviation caused by



(a) Plot of $\langle x \rangle$ against n



(b) Plot of σ_x against n

FIG. 3: Plots of position expectation value and uncertainties for each eigenstate n.

the addition of a constant factor $\frac{\mathcal{E}_0 a}{2}$, which can be thought of as a first order correction that takes into account that the 'average' energy is higher now. However, as we approach higher energy eigenstates, the results begin to coincide. In general, the n^2 pattern is roughly followed although not exactly for initial states, where the effect of the electric field is most pronounced.

To make the nature of these deviations for lower energy states, we can consider a higher

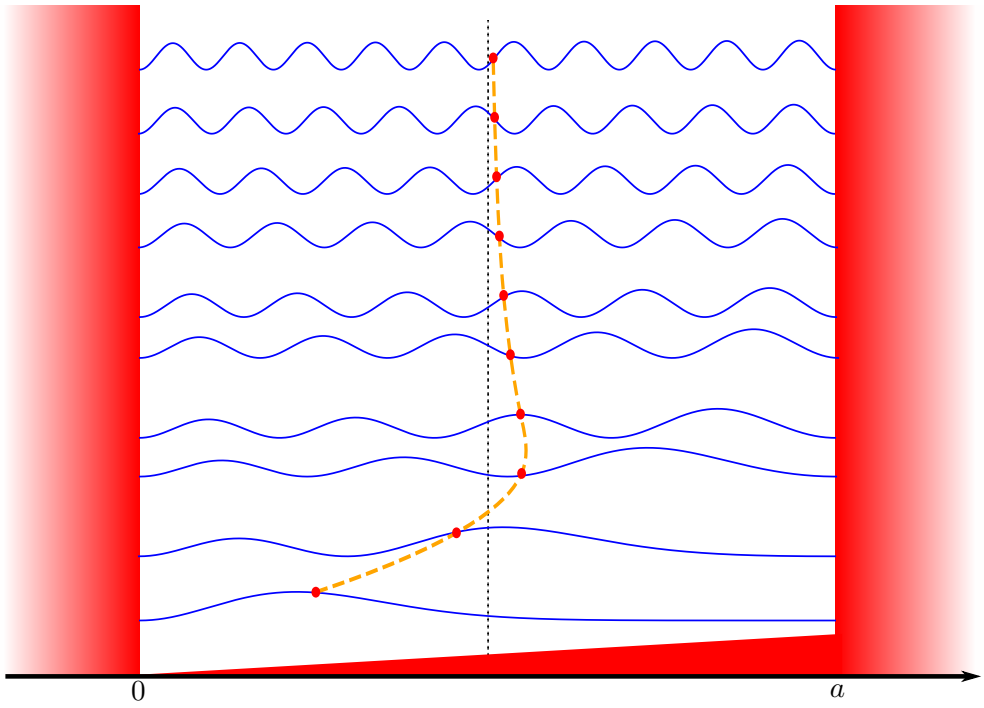


FIG. 4: Plot of position expectations with probability densities

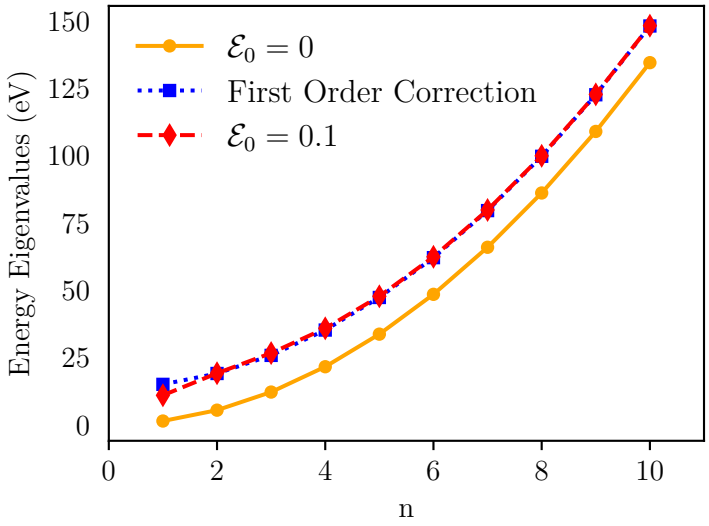
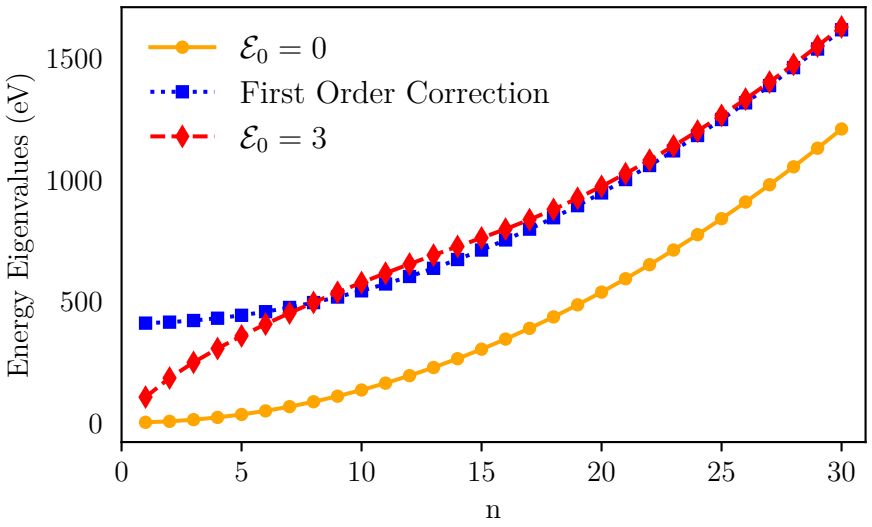
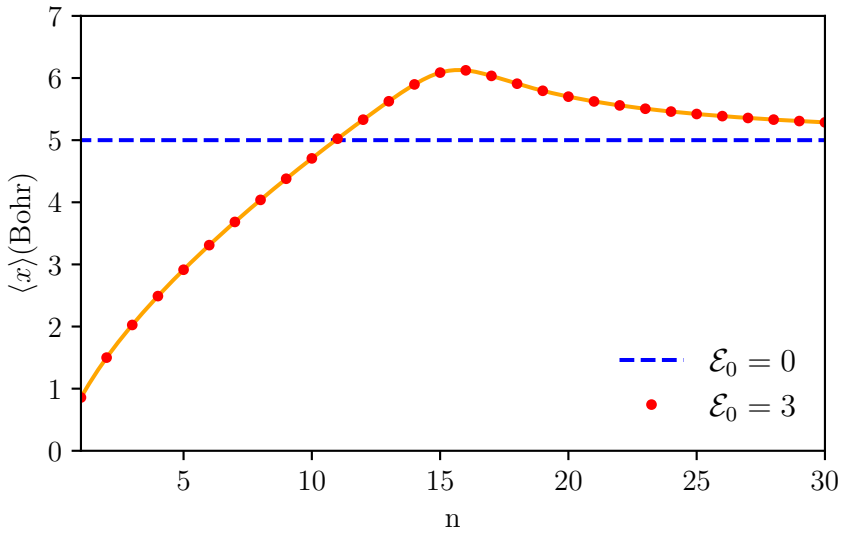


FIG. 5: Plot of energies with and without electric field

$\mathcal{E}_0$ value to make the effects more pronounced. For this we take $\mathcal{E}_0 = 3$ and plot both the energies and position expectation values in Fig. 6. This leads to some interesting observations and we can think of it in terms of a semi-classical description of the system: while the electron has an average position at the left hand side, with lower potential, its



(a) Plot of energy against n



(b) Plot of $\langle x \rangle$ against n

FIG. 6: Plots of energy and position expectation value for each eigenstate n.

energy is below the first order correction, as it spends longer confined in the region where the potential is lower. Similarly, when the expectation value is more to right, it has a higher energy as it spends more 'time' in the higher potential region. As the expectation value of position goes back to the center, the energies return to follow the n^2 trend almost exactly. This analogy is by no means exact, but gives us some insight into how the system tends to behave.

We can also change the value of $\mathcal{E}_0$ and plot the resulting graphs to see how the energy eigenvalues change depending on the tilt parameter in Fig. 7.

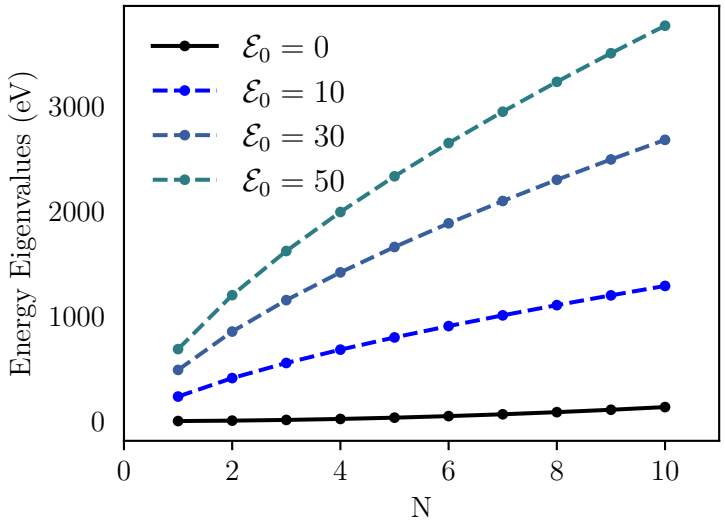


FIG. 7: Plot of energy eigenvalues for different values of $\mathcal{E}_0$

B. Convergence

Here, we check whether our basis states converge in a significant manner or not. To make this notion of convergence more concrete, we evaluate the behaviour of the following function of the number of basis states used

$$\Delta E(N) = \sum_{i=1}^{N} |\varepsilon_i^{(N+1)} - \varepsilon_i^{(N)}| \tag{21}$$

where $\varepsilon_i^{(N)}$ is the energy of the i^{th} state calculated using N basis states.

As we can see from Fig. 8, the differences between the eigenvalues become smaller and smaller as we increase the number of states N, so overall our energy eigenvalues converge.

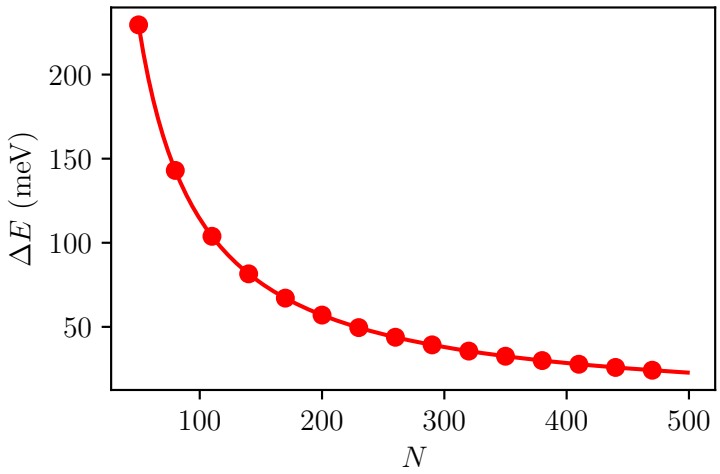


FIG. 8: Plot of ΔE against the number of basis states N, with every 30^{th} point marked

C. Dipole Moment and Applications

Although this technique is mostly useful as a pedagogical tool, there are some other areas in which it could successfully be employed. As discussed earlier, one particular use case is to find out how the optical spectrum of a potential well can be controlled using the gradient of the tilt. This can be useful if a tilted potential well is used to model a single electron transistor [6], where the ability to control the spectrum can allow us to set the threshold current.

Additionally, using the calculated eigenstates and eigenvalues, we can easily find the dipole matrix elements for the tilted potential well

$$\beta_{mn} \triangleq \langle \psi_m | \hat{x} | \psi_n \rangle \, .$$

Here, we have computed the matrix elements for some states numerically for both the infinite well as well as the modified system (with $\mathcal{E}_0 = 0.1$). These matrices have been calculated in the Debye units, where 0 to 11D are the values that dipole moments of simple diatomic molecules range from. The debye is a CGS unit of electric dipole moment, which is useful since it is very convenient to represent molecular dipole moments [7].

Here the absolute values of the dipole matrix elements of transitions between the first 10 states are given, with the diagonal elements, again, set to 0 to avoid clutter.

$$|d_{mn}| = \begin{pmatrix} 0.00 & 4.54 & 0.00 & 0.36 & 0.00 & 0.10 & 0.00 & 0.04 & 0.00 & 0.02 \\ & 0.00 & 4.90 & 0.00 & 0.46 & 0.00 & 0.14 & 0.00 & 0.06 & 0.00 \\ & & 0.00 & 5.00 & 0.00 & 0.50 & 0.00 & 0.16 & 0.00 & 0.07 \\ & & & 0.00 & 5.04 & 0.00 & 0.53 & 0.00 & 0.17 & 0.00 \\ & & & & 0.00 & 5.06 & 0.00 & 0.54 & 0.00 & 0.18 \\ & & & & & 0.00 & 5.08 & 0.00 & 0.54 & 0.00 \\ & & & & & & 0.00 & 5.08 & 0.00 & 0.55 \\ & & & & & & & 0.00 & 5.09 & 0.00 \\ & & & & & & & & 0.00 & 5.09 \\ & & & & & & & & & 0.00 \end{pmatrix}$$

$$|\beta_{mn}| = \begin{pmatrix} 0.00 & 2.83 & 0.86 & 0.43 & 0.23 & 0.14 & 0.09 & 0.06 & 0.04 & 0.03 \\ & 0.00 & 4.17 & 0.85 & 0.45 & 0.17 & 0.14 & 0.06 & 0.06 & 0.03 \\ & & 0.00 & 4.80 & 0.50 & 0.48 & 0.10 & 0.15 & 0.04 & 0.07 \\ & & & 0.00 & 4.99 & 0.29 & 0.51 & 0.06 & 0.17 & 0.02 \\ & & & & 0.00 & 5.05 & 0.19 & 0.53 & 0.04 & 0.18 \\ & & & & & 0.00 & 5.07 & 0.14 & 0.54 & 0.03 \\ & & & & & & 0.00 & 5.08 & 0.10 & 0.55 \\ & & & & & & & 0.00 & 5.09 & 0.08 \\ & & & & & & & & 0.00 & 5.09 \\ & & & & & & & & & 0.00 \end{pmatrix}$$

We can see that the selection rules that applied to the original system no longer hold, as the symmetry has been broken through the introduction of the tilt.

After finding the dipole moment, we proceed to plotting a spectrum for transitions under incident light. To do this we will consider each pair of states (up till some n^{th} state) and plot the respective energy difference along the x-axis and the intensity of the transition (given by the square of the dipole matrix element) on the y-axis. We obtain the plot in Fig. 9 for $n = 10$.

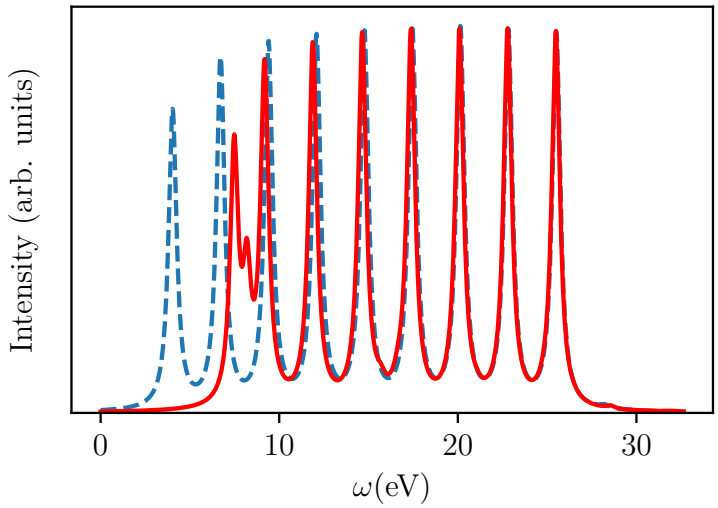


FIG. 9: Spectrum for transitions between the first 10 states

VII. SUMMARY

The tilted potential well is a hard problem to study analytically, but a thorough investigation provides us with some interesting and unintuitive results, that can be a great tool for teaching quantum mechanics. This method in particular can be particularly beneficial as it also grants exposure to students as to how we can use the matrix formulation of quantum mechanics as a basis for computational analysis. These ideas are used by computational and condensed matter physicists in routine but can be hard to motivate at the beginning, and this paper aims to provide both the motivation, as well as the guidance as to how this can be achieved. The tilted potential well is a fascinating system, and may potentially be something that we can use to model particular devices such as single electron transistors [6]. In addition, once students have familiarity with this method, they can experiment with it further as, because of the fact that it can reliably calculate bound states for any potential, it enables a variety of application, such as demonstrating band structures in periodic potentials [8].

Appendix A: Calculation of d_{mn}

We can evaluate d_{mn} by integration. When $m = n$, we have:

$$d_{nn} = \langle \phi_n \,|\, x \,|\, \phi_n \rangle \tag{22}$$

$$d_{nn} = \int dx\, x |\phi_n(x)|^2 \tag{23}$$

$$d_{nn} = \int_0^a dx\, x \left(\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \right)^2 \tag{24}$$

$$d_{nn} = \frac{2}{a} \int_0^a dx\, x \sin^2\left(\frac{n\pi x}{a}\right) \tag{25}$$

We will use a trigonometric identity to simply the equation

$$\sin^2(\theta) = \frac{1 - \cos(2\theta)}{2}. \tag{26}$$

We can use this to write

$$d_{nn} = \frac{2}{a} \int_0^a dx\, x \left(\frac{1 - \cos\left(\frac{2n\pi x}{a}\right)}{2} \right) \tag{27}$$

$$d_{nn} = \frac{1}{a} \int_0^a dx\, x - \frac{1}{a} \int_0^a dx\, x \cos\left(\frac{2n\pi x}{a}\right) \tag{28}$$

The first integral is easy:

$$\frac{1}{a} \int_0^a dx\, x = \frac{1}{2a} x^2 \Big|_0^a = \frac{a}{2} \tag{29}$$

For the other one we will use integration by parts:

$$\frac{1}{a} \int_0^a dx\, x \cos\left(\frac{2n\pi x}{a}\right) = \left[\frac{ax}{2n\pi} \sin\left(\frac{2n\pi x}{a}\right) + \frac{a^2}{4n^2\pi^2} \cos\left(\frac{2n\pi x}{a}\right) \right]_0^a \tag{30}$$

$$= \frac{a^2}{2n\pi} \sin\left(\frac{2n\pi a}{a}\right) + \frac{a^2}{4n^2\pi^2} \cos\left(\frac{2n\pi a}{a}\right) - \frac{a^2}{4n^2\pi^2} \tag{31}$$

$$= \frac{a^2}{2n\pi} \sin(2n\pi) + \frac{a^2}{4n^2\pi^2} \left(\cos(2n\pi) - 1\right) \tag{32}$$

$$= 0 + \frac{a^2}{4n^2\pi^2} (1 - 1) \tag{33}$$

$$= 0 \tag{34}$$

So we have:

$$d_{nn} = \frac{a}{2} \tag{35}$$

Similarly d_{mn}, when $m \neq n$, can be found by integration:

$$d_{mn} = \langle \phi_m \,|\, x \,|\, \phi_n \rangle \tag{36}$$

$$d_{mn} = \int dx\, \phi_m(x) x \phi_n(x) \tag{37}$$

$$d_{mn} = \frac{2}{a} \int_0^a dx\, x \sin\left(\frac{m\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) \tag{38}$$

We will use a trigonometric identity to simply the equation:

$$\sin(a)\sin(b) = \tfrac{1}{2}(\cos(a-b) - \cos(a+b)) \tag{39}$$

Using this,

$$d_{mn} = \frac{1}{a} \int_0^a dx\, x \left(\cos\left(\frac{(m-n)\pi x}{a}\right) - \cos\left(\frac{(m+n)\pi x}{a}\right)\right) \tag{40}$$

$$d_{mn} = \frac{1}{a} \left[\int_0^a dx\, x \cos\left(\frac{(m-n)\pi x}{a}\right) - \frac{1}{a}\int_0^a dx\, x \cos\left(\frac{(m+n)\pi x}{a}\right)\right] \tag{41}$$

We define:

$$k = \frac{(m-n)\pi}{a} \tag{42}$$

and

$$k' = \frac{(m+n)\pi}{a} \tag{43}$$

This makes our desired quantity:

$$d_{mn} = \frac{1}{a} \left[\int_0^a dx\, x \cos(kx) - \int_0^a dx\, x \cos(k'x)\right] \tag{44}$$

Through integration by parts:

$$\int_0^a dx\, x \cos(cx) = \left[\frac{x}{c}\sin(cx) + \frac{1}{c^2}\cos(cx)\right]_0^a \tag{45}$$

$$= \frac{a}{c}\sin(ca) + \frac{1}{c^2}\cos(ca) - 0 - \frac{1}{c^2}\cos(0) \tag{46}$$

$$= \frac{a}{c}\sin(ca) + \frac{1}{c^2}\cos(ca) - \frac{1}{c^2} \tag{47}$$

$$= \frac{ac\sin(ca) + cos(ca) - 1}{c^2} \tag{48}$$

So we have

$$d_{mn} = \frac{1}{a}\left[\frac{ak\sin(ka) + cos(ka) - 1}{k^2} - \frac{ak'\sin(k'a) + cos(k'a) - 1}{k'^2}\right]. \tag{49}$$

Now we can input values for k and k':

$$d_{mn} = \frac{1}{a}\frac{(m-n)\pi\sin((m-n)\pi) + \cos((m-n)\pi) - 1}{\frac{(m-n)^2\pi^2}{a^2}} - \frac{1}{a}\frac{(m+n)\pi\sin((m+n)\pi) + \cos((m+n)\pi) - 1}{\frac{(m+n)^2\pi^2}{a^2}} \tag{50}$$

$$d_{mn} = \frac{a}{\pi^2}\frac{(m-n)\pi\sin((m-n)\pi) + \cos((m-n)\pi) - 1}{(m-n)^2} - \frac{a}{\pi^2}\frac{(m+n)\pi\sin((m+n)\pi) + \cos((m+n)\pi) - 1}{(m+n)^2} \tag{51}$$

Here, $m-n$ and $m+n$ are integers so $\sin((m-n)\pi = \sin((m+n)\pi) = 0$.

$$d_{mn} = \frac{a}{\pi^2}\left[\frac{\cos((m-n)\pi) - 1}{(m-n)^2} - \frac{\cos((m+n)\pi) - 1}{(m+n)^2}\right] \tag{52}$$

and since $m-n$ and $m+n$ are integers so $\cos((m-n)\pi) = (-1)^{m-n}$ and $\cos((m+n)\pi) = (-1)^{m+n}$. It is easy to show, however that these will be equal since $(-1)^{2k} = 1$.

$$(-1)^{m+n} = (-1)^{m-n+2n} = (-1)^{m-n}(-1)^{2n} = (-1)^{m-n} \tag{53}$$

This leaves us with:

$$d_{mn} = \frac{a}{\pi^2}\left[\frac{(-1)^{m+n} - 1}{(m-n)^2} - \frac{(-1)^{m+n} - 1}{(m+n)^2}\right] \tag{54}$$

$$d_{mn} = \frac{a((-1)^{m+n} - 1)}{\pi^2}\left[\frac{1}{(m-n)^2} - \frac{1}{(m+n)^2}\right] \tag{55}$$

Clearly, when $m+n$ is even, d_{mn} will be 0. Otherwise:

$$d_{mn} = \frac{-2a}{\pi^2}\left[\frac{1}{(m-n)^2} - \frac{1}{(m+n)^2}\right] \tag{56}$$

$$d_{mn} = \frac{-2a}{\pi^2}\left[\frac{(m+n)^2 - (m-n)^2}{(m-n)^2(m+n)^2}\right] \tag{57}$$

$$d_{mn} = \frac{-2a}{\pi^2}\left[\frac{m^2+n^2+2mn - m^2 - n^2 + 2mn}{(m-n)^2(m+n)^2}\right] \tag{58}$$

$$d_{mn} = \frac{-2a}{\pi^2}\left[\frac{4mn}{(m^2-n^2)^2}\right] \tag{59}$$

$$d_{mn} = \frac{-8a}{\pi^2}\left[\frac{mn}{(m^2-n^2)^2}\right] \tag{60}$$

This leaves us with the following expression for the (non-diagonal) dipole matrix elements:

$$d_{mn} = \left[\frac{-8a}{\pi^2}\left(\frac{mn}{(m^2-n^2)^2}\right)\right]_{m+n \text{ is odd}} \tag{61}$$

[1] D. Griffiths and D. Schroeter, *Introduction to Quantum Mechanics* (Cambridge University Press, 2018).

[2] J. N. Churchill and F. O. Arntz, The infinite tilted-well: An example of elementary quantum mechanics with applications toward current research, American Journal of Physics **37**, 693 (1969), https://doi.org/10.1119/1.1975775.

[3] T. Ihn, *Semiconductor Nanostructures: Quantum states and electronic transport* (Oxford University Press, 2009).

[4] F. Marsiglio, The harmonic oscillator in quantum mechanics: A third way, American Journal of Physics **77**, 253 (2009), https://doi.org/10.1119/1.3042207.

[5] W. Ayub, Matrix mechanics, `https://github.com/WahajAyub/matrixmechanics` (2021).

[6] D. Dragoman and M. Dragoman, Tunneling devices, in *Encyclopedia of Condensed Matter Physics*, edited by F. Bassani, G. L. Liedl, and P. Wyder (Elsevier, Oxford, 2005) pp. 269–277.

[7] G. M. Barrow, *Physical Chemistry, 2nd Edition* (McGraw Hill, 1966).

[8] F. Le Vot, J. J. Meléndez, and S. B. Yuste, Numerical matrix method for quantum periodic potentials, American Journal of Physics **84**, 426 (2016), https://doi.org/10.1119/1.4944706.