Tamm-Davydov Algorithm

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Abstract

The Hamiltonian operator of a one-dimensional nonrelativistic quantum system, consisting of a particle of mass m subjected to a periodic potential energy $V(x)$ in the coordinate x, admits exclusively eigenfunctions in the improper sense. In this work, we show that a sufficient condition for the Hamiltonian to be endowed with eigenfunctions in the proper sense is constituted by a suitable local violation of the periodicity of the function $V(x)$.

1 Periodic Potential. Bloch Theorem

Let S_q be a non-relativistic quantum system consisting of a particle of mass m constrained to move on the x-axis, the seat of a conservative force field and periodic potential energy $V(x)$ with period $a > 0$: $V(x + na) \equiv V(x)$, $\forall n \in \mathbb{Z}$. Abstracting from the spin degrees of freedom, the Hilbert space associated with S_q is $\mathcal{H} = \mathcal{L}^2(\mathbb{R})$ and therefore, the Hamiltonian of the particle is

$$\hat{H}_0 = \frac{\hat{p}^2}{2m_e} + V(\hat{x}) \tag{1}$$

In the x-representation:

$$\hat{H}_0 \doteq -\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2} + V(x) \tag{2}$$

By Bloch's theorem [1], the eigenfunctions of $\hat{H}_0$ (i.e. of the energy) are:

$$u_k(x) = \varphi_k(x)\, e^{ikx} \tag{3}$$

where $k \in \mathbb{R}$ is the quasi-momentum of the particl [1] and $\varphi_k(x)$ is a periodic function with period $a > 0$. In other words, the energy eigenfunctions are amplitude-modulated plane waves with a periodic modulation envelope with the same period as the potential (*Bloch waves*). It follows that the operator (1) admits only eigenfunctions in the improper sense, so its spectrum $\sigma\left(\hat{H}_0\right)$ is purely continuous. The corresponding eigenvalues depend on k which therefore represents a good quantum number:

$$\hat{H}_0 u_k(x) = \varepsilon(k)\, u_k(x) \tag{4}$$

More precisely, $\sigma\left(\hat{H}_0\right)$ has a band structure [2]:

$$\sigma\left(\hat{H}_0\right) = \bigcup_\alpha \sigma_\alpha\left(\hat{H}_0\right)$$

which in general are disjoint $\sigma_\alpha\left(\hat{H}_0\right) \cap \sigma_{\alpha'}\left(\hat{H}_0\right) = \emptyset$ and separated by forbidden intervals (gaps). Without loss of generality, consider a potential $V(x)$ such that $\sigma\left(\hat{H}_0\right)$ consists of a single band. A notable one-dimensional case [3] is one in which the only conduction band is:

$$\varepsilon(k) = E_0 - 2\Delta\cos(ka) \tag{5}$$

with $0 < \Delta < E_0/2$ and these parameters have the dimensions of an energy. The function (5) is periodic with period $2\pi/a$, so it is sufficient to consider its restriction to the interval $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$ which in solid state physics is called the *first Brillouin zone*. In Fig. 1 we report the graph of $\varepsilon(k)$, from which we see that the width of the band is 4Δ.

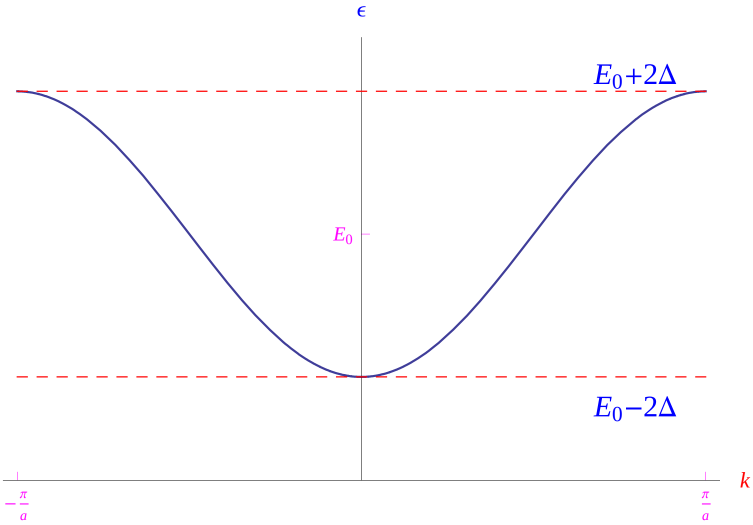

Figure 1: Trend of the function (5).

2 The Born-Von Karman conditions

In applications to solid state physics, we consider an "effective" segment of length $L = Na$, where $N \in \mathbb{N} \backslash \{0\}$, and then apply the Born-Von Karman (BVK) conditions which consist in replicating the segment of length L infinitely many times by imposing the connection condition:

$$u_k(x + Na) = u_k(x) \tag{6}$$

Taking into account the (3)and the periodicity of $\varphi_k(x)$:

$$e^{ikNa} = 1 \Longleftrightarrow \cos(kNa) = 1 \Longleftrightarrow k = \frac{2\pi}{Na} l \overset{def}{=} k_l, \quad \forall l \in \mathbb{Z}$$

$k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$ so assuming N is even:

$$k_l = \frac{2\pi}{Na} l, \quad l = -\frac{N}{2}, -\frac{N}{2} + 1, ..., 0, ..., \frac{N}{2} - 1, \frac{N}{2} \tag{7}$$

that is, the quasi-momentum of the particle can only assume N discontinuous values. The uniform decomposition of the first Brillouin zone follows:

$$\left[-\frac{\pi}{a}, \frac{\pi}{a}\right] = \bigcup_{l=-N/2}^{l=N/2} [k_l, k_{l+1}]$$

From (5):

$$\varepsilon_l = \varepsilon(k_l) = E_0 - 2\Delta \cos(k_l a) = E_0 - 2\Delta \cos\left(\frac{2\pi}{N} l\right) \tag{8}$$
$$l = -\frac{N}{2}, -\frac{N}{2} + 1, ..., 0, ..., \frac{N}{2} - 1, \frac{N}{2}$$

By (5) we have $\varepsilon(k) \equiv \varepsilon(-k)$ and since $k_{-l} = -k_l \Longrightarrow \varepsilon_{-l} = \varepsilon_l$, i.e. the discretization preserves the double degeneracy of the continuous spectrum of $\hat{H}_0$. In Fig. 2 we report the case $N = 10$.

Notation 1 *The discretization of $\sigma\left(\hat{H}_0\right)$ is not a quantization in the physical sense of the term, since it is generated by the BVKs or by a mathematical artifice to be able to reconstruct the periodicity of $V(x)$ in a way that does not invalidate Bloch theorem. It follows that the discrete values (eq. 8) are not energy levels of a bound system. In fact, each of them corresponds to a Bloch wave, therefore an eigenfunction in an improper sense. Therefore, the degeneracy of the discrete levels should not be surprising, while in the case of a one-dimensional bound system, the discrete spectrum of the Hamiltonian is never degenerate by virtue of the Wronskian theorem [4].*

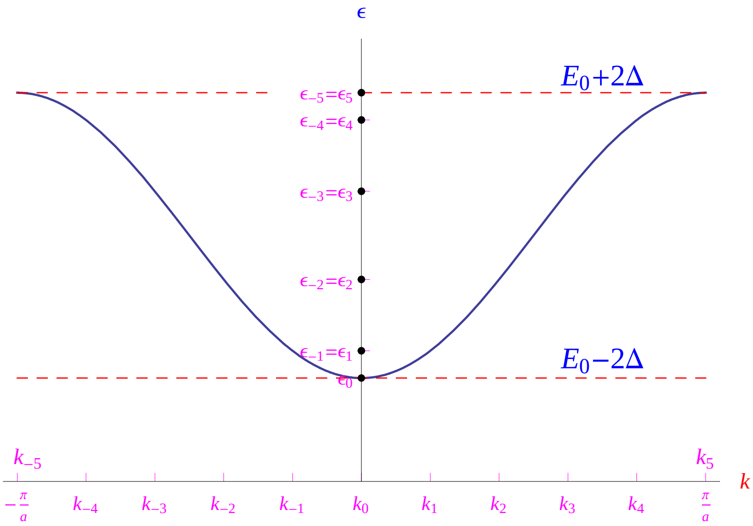

Figure 2: Discretization of energy levels for $N = 10$.

3 Local periodicity violation

A local violation of the periodic behavior of the potential $V(x)$ is represented by a potential energy term $w(x-\xi)$ appreciably different from zero only in a neighborhood of the point $\xi \in (n_0 a, (n_0+1)a)$ for a given $n_0 \in \mathbb{Z}$ think of a Gaussian centered at ξ). It follows that in the time-independent perturbation theory, the Hamiltonian (1) plays the role of unperturbed Hamiltonian (for $|w(x-\xi)| \ll V(x)$), then setting:

$$\hat{H} = \hat{H}_0 + \hat{w} \tag{9}$$

In Dirac notation, the eigenvalue equation for $\hat{H}_0$, is written:

$$\hat{H}_0 |k\rangle = \varepsilon(k) |k\rangle \tag{10}$$

Applying the BVK i.e. discretizing:

$$\hat{H}_0 |k_l\rangle = \varepsilon_{k_l} |k_l\rangle, \quad l = -\frac{N}{2}, -\frac{N}{2}+1, ..., 0, ..., \frac{N}{2}-1, \frac{N}{2} \tag{11}$$

resulting in $|k_l\rangle \in \mathcal{H}^{(N)}$, the latter being the subspace of $\mathcal{H}$ subtended by N, so $\lim_{N\to+\infty} \mathcal{H}^{(N)} = \mathcal{H}$. In the x-representation:

$$u_{k_l}(x) = \langle x|k_l\rangle = \varphi_{k_l}(x) e^{ik_l x} \tag{12}$$

The system of N vectorsi $\{|k_l\rangle\}$ is a complete orthonormal system in $\mathcal{H}^{(N)}$:

$$\sum_{k_l=-\pi/a}^{\pi/a} |k_l\rangle\langle k_l| = \hat{1}^{(N)}, \quad \langle k_l|k_l'\rangle = \delta_{k_l,k_l'} \tag{13}$$

where $\hat{1}^{(N)}$ is the identity operator in $\mathcal{H}^{(N)}$. If $\hat{1}$ is the identity operator in $\mathcal{H}$

$$\lim_{N\to+\infty} \hat{1}^{(N)} = \hat{1} = \int_{-\infty}^{+\infty} dk\, |k\rangle\langle k|$$

Given this, the eigenvalue equation for the Hamiltonian (9) has the form:

$$\hat{H}|\tilde{u}\rangle = W|\tilde{u}\rangle \tag{14}$$

where $|\tilde{u}\rangle$ are the eigenkets of the energy in the presence of the perturbative term $w(x-\xi)$, and $W \in \mathbb{R}$the corresponding eigenvalues. Since $\{|k_l\rangle\}$ is a basis of $\mathcal{H}^{(N)}$ we can expand $|\tilde{u}\rangle$ as a linear combination of the eigenvalues $|k_l\rangle$:

$$|\tilde{u}\rangle = \sum_{k_l=-\pi/a}^{\pi/a} c_{k_l}|k_l\rangle, \quad c_{k_l} = \langle k_l|\tilde{u}\rangle \tag{15}$$

Let's rewrite (14)

$$\left(\hat{H}_0 + \hat{w}\right)\sum_{k_l} c_{k_l}|k_l\rangle = W\sum_{k_l} c_{k_l}|k_l\rangle \Longrightarrow \sum_{k_l} c_{k_l}\varepsilon_{k_l}|k_l\rangle + \sum_{k_l} c_{k_l}\hat{w}|k_l\rangle = W\sum_{k_l} c_{k_l}|k_l\rangle$$

Multiplying by $\langle k_l'|$

$$\underbrace{\sum_{k_l} c_{k_l}\varepsilon_{k_l}\delta_{k_l'k_l}}_{=c_{k_l'}\varepsilon_{k_l'}} + \sum_{k_l} c_{k_l}\underbrace{\langle k_l'|\hat{w}|k_l\rangle}_{w_{k_l'k_l}} = W\underbrace{\sum_{k_l} c_{k_l}\delta_{k_l'k_l}}_{c_{k_l'}}$$

So

$$\left(W - \varepsilon_{k_l'}\right)c_{k_l'} = \sum_{k_l=-\pi/a}^{\pi/a} c_{k_l}w_{k_l'k_l} \tag{16}$$

which is a system of N algebraic equations in W. Let us make explicit the matrix elements of the perturbative term. To this end, we observe that in the x-representation the unitary operator $\hat{1}^{(N)}$ of $\mathcal{H}^{(N)}$ is $\int_{n_0a}^{(n_0+1)a} dx\,|x\rangle\langle x| = \hat{1}^{(N)}$ so denoting with $\cdot$ the Hermitian product in $\mathcal{H}^{(N)}$:

$$w_{k_l'k_l} = \langle k_l'|\hat{w}|k_l\rangle = \left(\langle k_l'|\,\hat{w}\right)\cdot\left(\int_{n_0a}^{(n_0+1)a} dx\,|x\rangle\langle x|\right)\cdot|k_l\rangle = \langle k_l'|\int_{n_0a}^{(n_0+1)a} dx\,|x\rangle\underbrace{\langle x|\hat{w}|k_l\rangle}_{=w(x-\xi)\langle x|k_l\rangle}$$

i.e.

$$w_{k_l'k_l} = \int_{n_0a}^{(n_0+1)a} u_{k_l'}^*(x)\,w(x-\xi)\,u_{k_l}(x) \tag{17}$$

By the mean theorem:

$$\exists\xi' \in [n_0a, (n_0+1)a] \mid \int_{n_0a}^{(n_0+1)a} w(x-\xi)\,dx = \langle w\rangle a$$

where $\langle w \rangle = w(\xi' - \xi)$ is the integral mean (i.e. the average value) of $w(x-\xi)$ at $[n_0 a, (n_0+1)a]$. Since $w(x-\xi)$ is an extremely sharp momentum around ξ, we expect $\xi' \sim \xi$. Assuming $u_{k_l}(x)$ to be appreciably constant in $(n_0 a, (n_0+1)a)$, we have by (17)

$$w_{k_l' k_l} \simeq u_{k_l'}^* (\xi') \, u_{k_l} (\xi') \langle w \rangle a \tag{18}$$

Performing the change of variable $x' = x - \xi'$:

$$w_{k_l' k_l} = u_{k_l'}^* (0) \, u_{k_l} (0) \langle w \rangle a \tag{19}$$

which replaced in (16):

$$\left(W - \varepsilon_{k_l'}\right) c_{k_l'} = u_{k_l'}^* (0) \langle w \rangle a \underbrace{\sum_{k_l} c_{k_l} u_{k_l} (0)}_{(15) \Longrightarrow \tilde{u}(0)} = u_{k_l'}^* (0) \, \tilde{u} (0) \langle w \rangle a \tag{20}$$

so

$$c_{k_l'} = \frac{u_{k_l'}^* (0) \, \tilde{u} (0) \langle w \rangle a}{W - \varepsilon_{k_l'}} \tag{21}$$

Replacing (21) in (16) and taking into account (19):

$$\sum_{k_l = -\pi/a}^{\pi/a} \frac{|u_{k_l}(0)|^2}{W - \varepsilon_{k_l}} = \frac{1}{a \langle w \rangle} \tag{22}$$

It is clearly evident $|u_{k_l}(0)|^2 = |\varphi_{k_l}(0)|^2 = b_{k_l} \simeq b > 0$,so the previous one becomes:

$$b \Phi (W) = \frac{1}{a \langle w \rangle} \tag{23}$$

having defined the real function of the real variable W:

$$\Phi (W) = b \sum_{k_l = -\pi/a}^{\pi/a} \frac{1}{W - \varepsilon_{k_l}} \tag{24}$$

(23) is therefore an algebraic equation in W of degree N, and therefore admits N roots which are the new eigenvalues of the energy. This equation must be solved graphically/numerically, distinguishing the two cases $\langle w \rangle > 0$ (potential barrier since $w(x-\xi) > 0$) and $\langle w \rangle < 0$ (potential well). Let us study the function (24) which is defined in $\mathbb{R} \backslash \bigcup_{k_l} \{\varepsilon_{k_l}\}$ on the whole real axis excluding the N points ε_{k_l}. The graph intersects the ordinate axis in $\Phi(0) = -b \sum_{k_l} \varepsilon_{k_l}^{-1} < 0$. It turns out then:

$$\lim_{W \to \varepsilon_{k_l}^-} \Phi (W) = -\infty, \quad \lim_{W \to \varepsilon_{k_l}^+} \Phi (W) = +\infty$$

so the graph has N vertical asymptotes. Furthermore

$$\lim_{W \to +\infty} \Phi (W) = 0^+, \quad \lim_{W \to -\infty} \Phi (W) = 0^-$$

By substituting (24) with (8) we obtain the graph of fig. (3) in the case $N = 10$. For $\langle w \rangle < 0$ the roots of (23) are arranged as in the graph of fig. 4, from which we see

$$W_0 \ll \varepsilon_0, \quad W_j \simeq \varepsilon_j, \quad j = 1, 2, 3, 4$$

In solid state physics is $N \sim 10^8$ so the set of levels approximates a continuous band. The result is that for $\langle w \rangle < 0$ the lowest level W_0 «detaches» from the continuous band. Fig. 5 illustrates the search for roots in the case where $w(x-\xi)$ is a potential barrier i.e. $\langle w \rangle > 0$. Here we see that

$$W_4 \gg \varepsilon_4, \quad W_j \simeq \varepsilon_j, \quad j = 0, 1, 2, 3$$

For each $N < +\infty$

$$\begin{aligned} \langle w \rangle < 0 &\Longrightarrow W_0 \ll \varepsilon_0, \quad W_j \simeq \varepsilon_j, \quad j = 1, 2, ..., N-1 \\ \langle w \rangle > 0 &\Longrightarrow W_{N-1} \gg \varepsilon_{N-1}, \quad W_j \simeq \varepsilon_j, \quad j = 0, 1, ..., N-2 \end{aligned}$$

For $N \to +\infty$, if $\langle w \rangle < 0$ the levels centered in W_0 (obtained for $N < +\infty$) «detach» from the continuous band, resulting more depressed in energy. If $\langle w \rangle > 0$ the levels centered in W_{N-1} (obtained for $N < +\infty$) «detach» from the continuous band, resulting in more energized excitement.

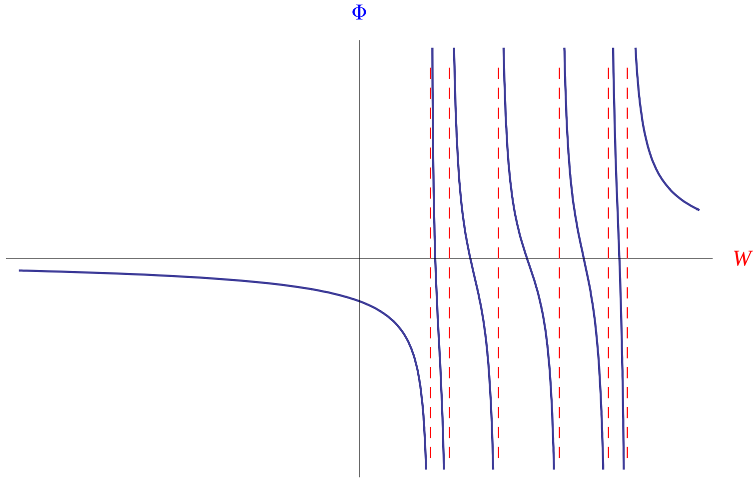

Figure 3: Trend of the function $\Phi(W)$.

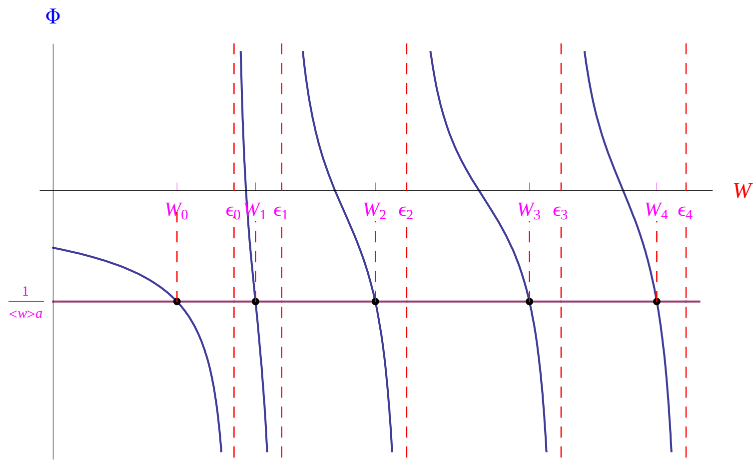

Figure 4: Roots of the equation (23) for $\langle w \rangle > 0$.

Let us move on to the determination of the perturbed eigenfunctions. In the coordinate x':

$$\tilde{u}_{k_l}(x') = \sum_{k'_l = -\frac{\pi}{a}}^{\pi/a} c_{k'_l} u_{k'_l}(x')$$

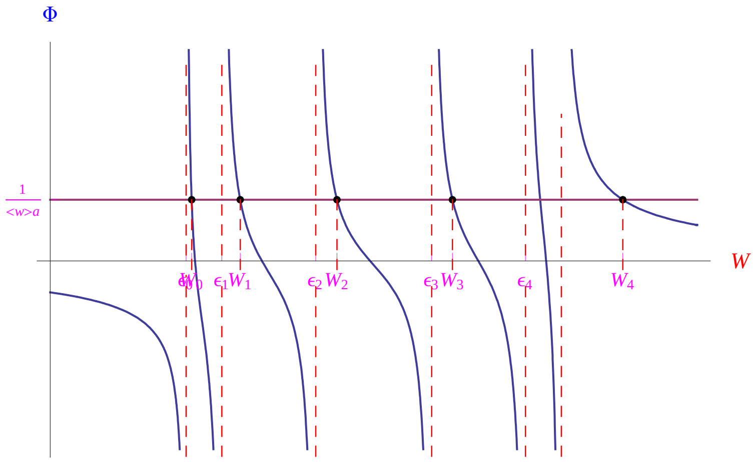

Figure 5: Roots of the equation (23) for $\langle w \rangle < 0$.

It must be $\hat{H}\tilde{u}_{k_l} = W_{k_l}\tilde{u}_{k_l}$. By (21)-(3):

$$\tilde{u}_{k_l}(x') = a\langle w \rangle \tilde{u}_{k_l}(0) \sum_{k'_l=-\frac{\pi}{a}}^{\pi/a} \frac{\varphi^*_{k'_l}(0)\,\varphi_{k'_l}(x')}{W_{k_l} - \varepsilon_{k'_l}} e^{ik'_l x'}$$

We observe that

$$\varphi^*_{k'_l}(0)\,\varphi_{k'_l}(x') \simeq \varphi^*_{k'_l}(0)\,\varphi_{k'_l}(0) = \left|\varphi_{k'_l}(0)\right|^2 \equiv \alpha_{k_l} > 0$$

Considering the real constants α_{k_l} to be independent of k_l i.e. $\alpha_{k_l} \equiv \alpha$, $\forall k_l \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$: $\varphi^*_{k'_l}(0)\,\varphi_{k'_l}(x') \simeq \alpha$. It follows

$$\tilde{u}_{k_l}(x') = a\langle w \rangle \beta_{k_l} \sum_{k'_l=-\frac{\pi}{a}}^{\pi/a} \frac{e^{ik'_l x'}}{W_{k_l} - \varepsilon_{k'_l}}$$

where $\beta_{k_l} \equiv \tilde{u}_{k_l}(0)\,\alpha$ and also considering this constant independent of k_l i.e. $\tilde{u}_{k_l}(0)\,\alpha \simeq \beta$, we finally get it

$$\tilde{u}_{k_l}(x') = a\langle w \rangle \beta \sum_{k'_l=-\frac{\pi}{a}}^{\pi/a} \frac{e^{ik'_l x'}}{W_{k_l} - \varepsilon_{k'_l}} \tag{25}$$

Let's start with the case $\langle w \rangle < 0$ (potential well). In fig. 6 we report the behavior of the probability amplitude$|\tilde{u}_0(x)|^2$ not normalized and in dimensionless units, from which we see that $\tilde{u}_0(x')$ is a bound state. More precisely, recalling that $x' = x - \xi'$, the particle is localized in the n_0-th interval $[n_0 a, (n_0+1)\,a]$. In fig. 7 we plot the graph of the eigenfunction $\tilde{u}_1(x)$, from which we see that it has the appearance of a Bloch wave, so the particle is not a bound state (delocalized particle). In fig. 8 we plot the graph of the eigenfunction $\tilde{u}_2(x)$; here too we see that it is a Bloch wave. Similar behavior for the remaining eigenfunctions.

Let's now move on to the case $\langle w \rangle > 0$ (potential barrier). In figs. 9-10-11-11 the graphs of $\tilde{u}_0(x'), \tilde{u}_1(x'), \tilde{u}_2(x'), \tilde{u}_3(x')$ which are now Bloch waves.

4 Physical interpretation of results

The physical interpretation is immediate: for $\langle w \rangle < 0$ we have a potential well, and $\tilde{u}_0(x)$ is the corresponding bound state. Mathematically, it is an eigenfunction of $\hat{H}$ in the proper sense. For

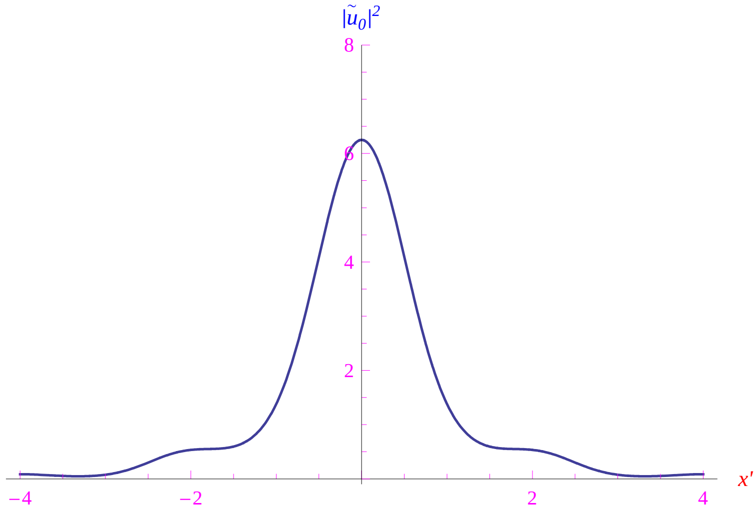

Figure 6: Andamento di $|\tilde{u}_0\,(x)|^2$ per $\langle w \rangle < 0$.

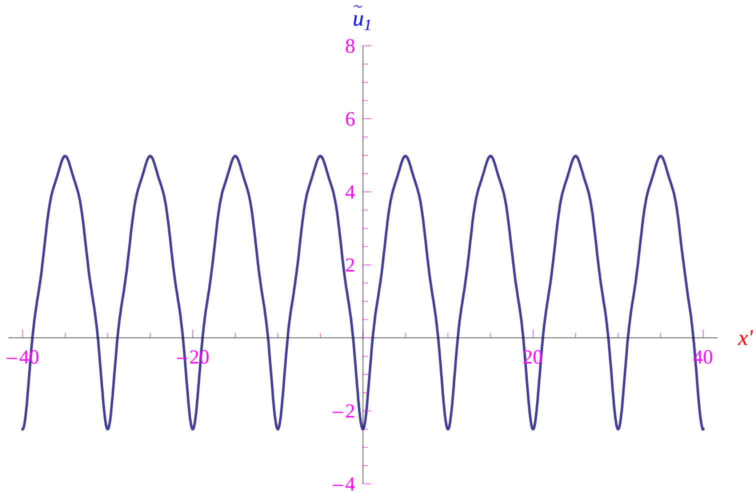

Figure 7: Trand of $\tilde{u}_1\,(x)\,,\ \langle w \rangle < 0$.

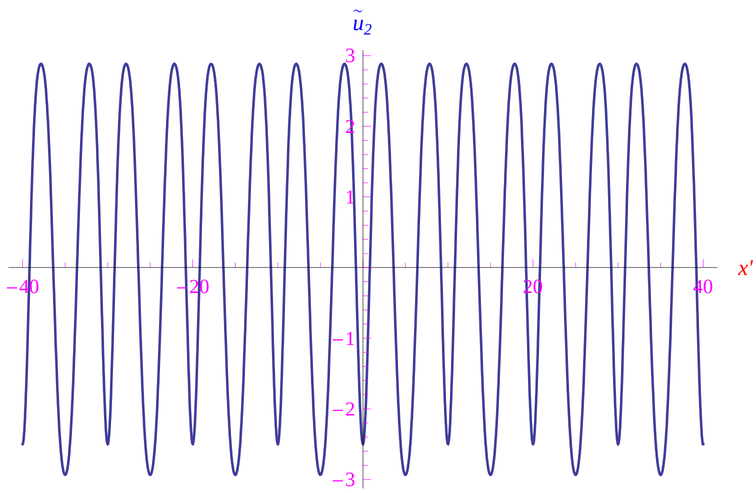

Figure 8: Trand of $\tilde{u}_2\,(x)\,,\ \langle w \rangle < 0$.

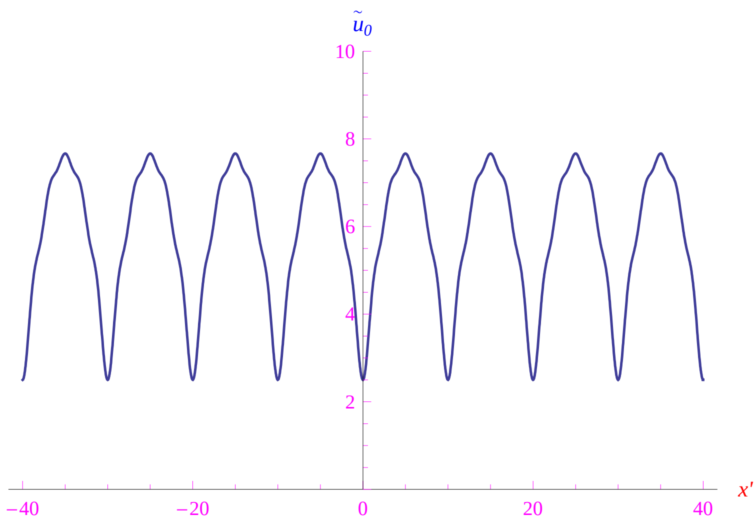

Figure 9: Trand of $\tilde{u}_0\left(x\right)$, $\langle w\rangle > 0$.

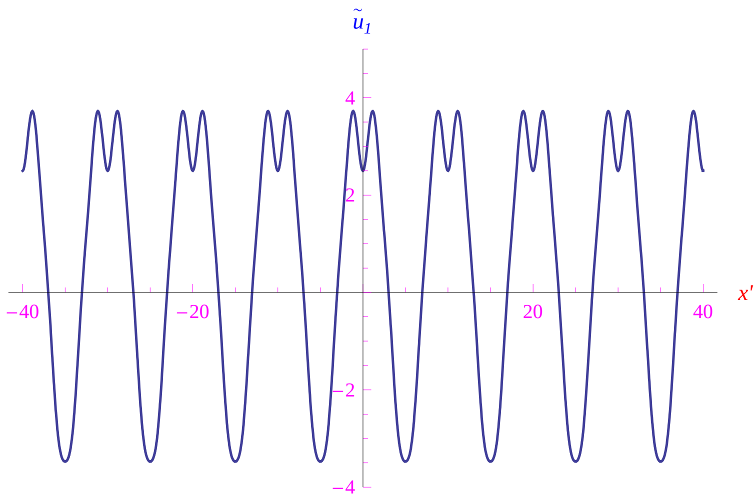

Figure 10: Trand of $\tilde{u}_1\left(x\right)$, $\langle w\rangle > 0$.

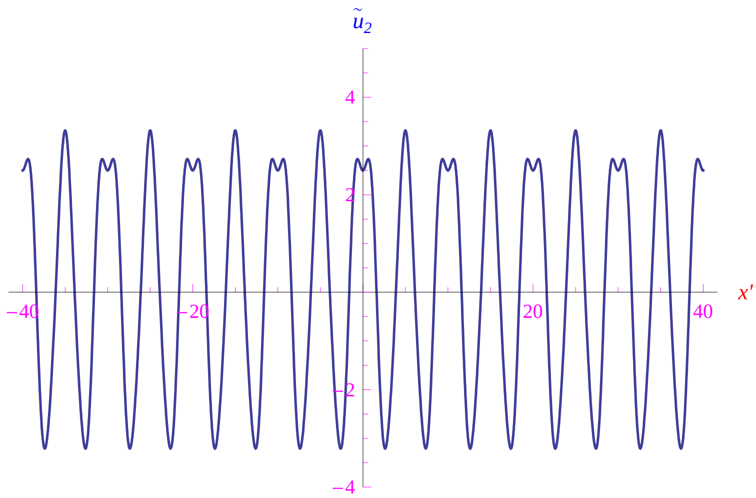

Figure 11: Trand of $\tilde{u}_2\left(x\right)$, $\langle w\rangle > 0$.

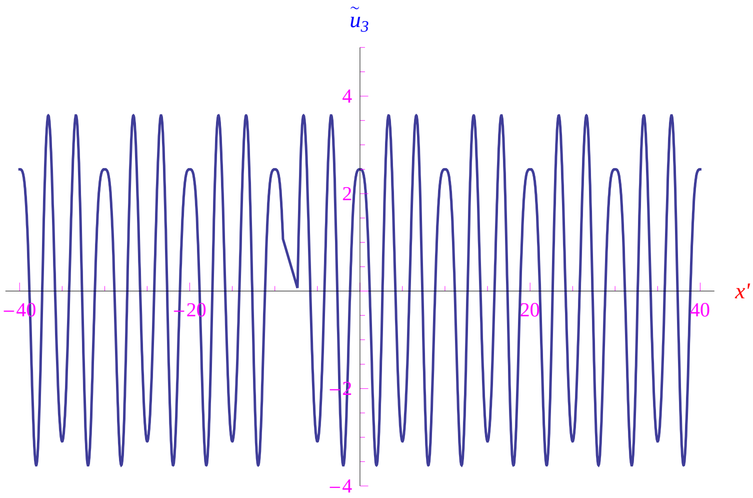

Figure 12: Trand of $\tilde{u}_3\,(x)\,,\,\langle w\rangle > 0.$

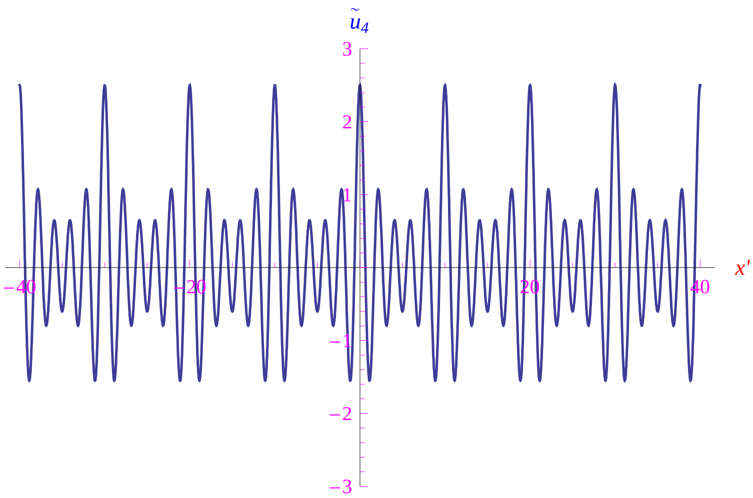

Figure 13: Trand of $\tilde{u}_4\,(x)\,,\,\langle w\rangle > 0.$

$\langle w \rangle < 0$ there are no bound states, since we now have a potential barrier and since we have assumed $|w(x-\xi)| \ll |V(x)|$, this barrier is penetrable through a tunneling process.

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