Journal of Mathematical Chemistry, Vol. 43, No. 1, January 2008 (© 2007)
DOI: 10.1007/s10910-006-9201-y

Effective potential, Bohm's potential plus classical potential, analysis of quantum transmission

María F. González and Xavier Giménez

Departament de Química Física, Universitat de Barcelona, Martí i Franquès, 1, 08028 Barcelona, Spain

Javier González and Josep Maria Bofill*

Department de Quimica Orgánica, Universitat de Barcelona, Martíi Franquès, 1, 08028 Barcelona, Spain
E-mail: jmbofill@ub.edu

María F. González, Javier González, Josep Maria Bofill, and Xavier Giménez

Centre Especial de Recerca en Química Teòrica, Parc Científic de Barcelona, Baldiri Reixac 10–12, 08028 Barcelona, Spain

Received 10 July 2006; accepted 16 September 2006

The influence of spreading, in wavepacket transmission across a potential barrier has been analyzed, by considering several collisions between a wavepacket and a potential barrier, in which the initial distance between the packet and the barrier—the launching distance, is changed. An effective total potential (Bohm's quantum potential plus classical potential), has been used, to show that, for suitable classical barrier widths and heights, light masses, as well as mean collision energies, one should expect an increase of the quantum transmission factor as the initial wavepacket—barrier distance is decreased. Numerically converged time-dependent wavepacket propagation calculations confirm that trend, leading to an increase as high as 20% per Å, in thin square and Eckart barrier problems. Possibilities of experimentally measuring this effect are also analyzed.

KEY WORDS: Wavepacket propagation, quantum transmission, tunnel effect, Bohmian mechanics, quantum hydrodynamics, time dependent discrete variable representation method

1. Introduction

The transmission of a particle across an external potential energy barrier is ubiquitous in theoretical studies of quantum systems, as a means of modeling a wealth of dynamical processes. In this regard, much work is devoted to

*Corresponding author.

one-dimensional treatments. The reason is that if one is able to select a proper adiabatic motion, for defining the external potential, as well as an adequate coordinate to display the transmission process, then it is found that the essential physics is often retained. It is much frequently the case, for instance, in optics, atomic and molecular physics, including chemical reactions, spectroscopy, as well as solid-state physics [1].

For several decades, the quantum transmission problem has been solved by means of tailored methods, based on the time-independent Schrödinger equation [2]. For simple model potentials, exact analytical solutions are available. On the other hand, numerically exact solutions, for virtually any other kind of potential profiles, have been obtained, leading to a nearly complete characterization of physical phenomena. Direct, compound (resonance) scattering, back-reflections, as well as several forms of tunneling, either static or dynamic, have been described to great accuracy [3].

More recently, efficient forms of time-dependent wavepacket (TDWP) methods have been developed [4]. However, envisioning transmission problems within the TD context adds new ingredients. For instance, the use of WP, in place of fixed-energy wavefunctions, brings one additional degree of freedom, namely specifying how a plane wave superposition is built up, so as to set the initial shape, width, and mean velocity of the packet. At this point, some questions emerge: does the WP shape, width, for a given mean translational energy, affect the transmission factor? Even more, does the well known, but usually ignored, phenomenon of WP spreading make any influence in this transmission factor? These are questions that, needless to say, are meaningless in the time-independent picture of dynamical processes. However, if the TDWP picture has any specific role to play, namely a more complete view to quantum motion, or a better definition of the quantum-classical correspondence, then the above issues have to be properly addressed.

Some years ago, Skodje and Truhlar [5] did a quite comprehensive study of WP propagation, showing that transmission across a potential barrier was dependent, for a given mean translational energy, on the shape, width, as well as, more surprisingly, on the initial launching distance, i.e., the $t = 0$ separation between the WP and barrier centers. However, an explanation for the latter of the above results was not given.

On another hand, Muga et al. [6] performed an analytical study of transmission processes, under delta-function barrier potentials, for a particular initial state chosen so far to allow for analytic integration of the transmission factor. A main result has been that no negative momenta, in the initial packet, contribute to transmission, along with the fact that, for sufficiently large initial distances, the transmission is independent of the initial location.

More recently, some of the authors performed a study of WP transmission across one–dimensional barriers, under the Bohmian perspective [7]. Their results strongly suggest that, when spreading is non-negligible, the transmission yields

the very same Skodje–Truhlar's effect. In other contexts, e.g., optics and particle physics, spreading has been given an important role. For instance, it has been argued that it should be taken into consideration for a proper account of CP violation [8].

The above phenomenon, namely the dependence of transmission on the initial particle–barrier distance, is intringuing. One may naively expect that the distance traveled as a free particle, i.e., as long as the particle packet does not overlap the target potential, does not affect any of its transmission properties. A classical-like interpretation tells that the particle experiences no force, so that it keeps moving at constant velocity, for the initial part of the trajectory, which is the part that changes, as the distance between the particle and the barrier is changed. However, quantum-mechanically it is well known that it is not the case. In this regard, the Bohmian view is very useful, for it shows (see below) that even the free particle, conveniently described by a WP, is subject to the quantum force. It may thus have some effect as, for instance, it is well known to be the origin of spreading. In any case, it is not clear under which conditions this effect is remarkable enough, so as to be taken into consideration.

Our wish, with the present work, is to provide a quantitative check of such phenomenon, as well as an analysis of its origin. To this purpose, the remainder of the paper is organized as follows: section 2 describes the theoretical approach, as well the method of computation for the transmission factors. Section 3 presents the results so far obtained, along with a discussion, that eventually focuses on some experimental possibilities of measuring the influence of spreading, in both molecular and electron conduction processes.

2. Theoretical approach and calculation method

One may state the present problem as follows: consider a system, or simply a particle, set to collide against an external potential barrier. Then our question is: under which conditions, if any, one may obtain that quantum transmission does depend on spreading? It may seem at first difficult to tackle directly the spreading phenomenon. However, the possibility of preparing and controlling WP, under well-defined spatial and temporal conditions, tells that one may get a measure of it, simply by studying the influence of the distance traveled as a free WP, in, e.g., transmission across an external potential barrier, for the spreading of a free gaussian WP is well known. Consequently, in the present work, we have put the influence of spreading in geometrical terms, so that the right question is whether the initial launching distance has any influence in the transmission factor.

To that purpose, the standard Schrödinger formulation readily brings some remarkable data. If one expands the initial, $t = 0$ WP, in terms of the true eigensolutions of the collision problem, one gets substantially different linear

combinations, as the initial packet is placed at different initial distances. This above statement may be better understood with the aid of figure 1, where the expansion coefficients, in terms of the energy eigenvalues, have been plotted for several initial launching distances, for a WP set to collide against a square potential barrier. It is observed that the coefficients describe the same overall trend, but the specific values for each initial distance appear to change, in some cases quite importantly. These changes are larger, the lower is the eigenvalue so far considered. This behavior may be explained on the basis that the lower eigenvalues are those most affected by the presence of the square barrier, in the sense that a lower frequency of the eigenstate facilitates perturbing it to larger distances away from the barrier.

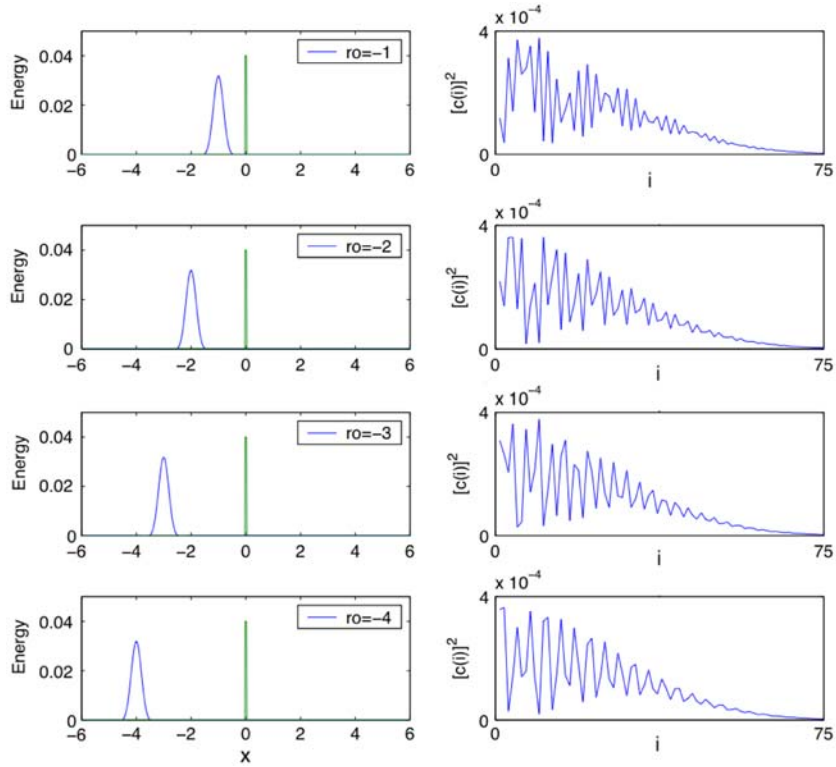

Figure 1. Left vertical panel: statement of the problem; four initial WP, at four different starting positions, set to collide against a square barrier. Blue trace: initial WP density. Green trace: a thin square barrier, the width being set small enough to maximize the tunneling transmission. r_0: initial launching distance, measured from the midpoint of the square barrier. Right vertical panel: square modulus of the expansion coefficient, as a function of the energy eigenvalue, for the corresponding (left) initial WP. Only the coefficients for the first 75 energy eigensolutions are shown. Eigenvalues are ordered according to increasing energy. Notice that the energy eigensolutions are *not* plane waves, but rather distorted plane waves owing to the perturbation caused by the square barrier.

Results from figure 1 are clear evidence that the transmission factor may change with the initial distance. This effect also evidences that none of the initial conditions might be regarded as asymptotic. This statement provides an initial clue for explaining the present results, since it is well known that a free evolving WP has an overlap with a plane wave (the asymptotic eigensolutions), which is independent of position.

This change in coefficients, however, describes a very complex pattern, so that it is not possible at this stage to extract any regularity, namely whether transmission increases with an increase in the distance, or the opposite. We have found instrumental, in order to get a deeper insight, recasting the transmission problem within Bohm's formulation of quantum mechanics [9]. As it is well known, this means that the TD Schrödinger equation is expressed as quantum hydrodynamics differential equations:

$$\frac{\partial S(\mathbf{x},t)}{\partial t}+\frac{(\nabla_{\mathbf{x}}S(\mathbf{x},t))^T(\nabla_{\mathbf{x}}S(\mathbf{x},t))}{2m}-\frac{h^2}{(8\pi^2 m)}\frac{\nabla_{\mathbf{x}}^2R(\mathbf{x},t)}{R(\mathbf{x},t)}+V(\mathbf{x})=0, \tag{1a}$$

$$\frac{\partial R^2(\mathbf{x},t)}{\partial t}+\nabla_{\mathbf{x}}^T\left(\frac{R^2(\mathbf{x},t)\nabla_{\mathbf{x}}S(\mathbf{x},t))}{m}\right)=0, \tag{1b}$$

where the superscript T means transposed, $R^2(\mathbf{x},t)$ is the density, $S(\mathbf{x},t)$ is the action, $\nabla_{\mathbf{x}}^T=(\partial/\partial x_1,\ldots,\partial/\partial x_N)$, and $\nabla_{\mathbf{x}}^2=\nabla_{\mathbf{x}}^T\nabla_{\mathbf{x}}=\partial^2/\partial x_1^2+\cdots+\partial^2/\partial x_N^2$, being N the dimension of the vector $\mathbf{x}$. Here, $R(\mathbf{x},t)$ and $S(\mathbf{x},t)$ are the real-amplitude function and the real-phase function, respectively, of the wave function solution of the TD Schrödinger equation. Equation (1), along with the so-called Bohm's guidance relation, $\nabla_{\mathbf{x}}S(\mathbf{x},t)=\mathbf{p}$, being $\mathbf{p}$ the linear momentum, puts explicit the strict formal equivalence between equation (1a) and the classical Hamilton–Jacobi equation. This equivalence permits to introduce in quantum mechanics trajectories, $\mathbf{x}=\mathbf{x}(t)$, pursued by points associated to particles of mass m, so-called also bohmian particles. According to Bohm's view, at each point of the space $(\mathbf{x},t)$, the tangent vector of the trajectory, $\mathrm{d}\mathbf{x}/\mathrm{d}t|_{\mathbf{x}=\mathbf{x}(t)}$, is equal to the vector field, $\mathbf{p}/m=m^{-1}\nabla_{\mathbf{x}}S(\mathbf{x},\tau)|_{\mathbf{x}=\mathbf{x}(t),\tau=t}$. Due to this fact, equation (1b) can be integrated easily by characteristics [10], using the above relation, $\mathrm{d}\mathbf{x}/\mathrm{d}t|_{\mathbf{x}=\mathbf{x}(t)}=\mathbf{p}/m$. After some trivial rearrangements, one obtains the well-known expression:

$$R^2(\mathbf{x},t)=R_0^2\exp\left(-\frac{1}{m_C}\int_{t_0}^{t}\nabla_{\mathbf{x}}^2S(\mathbf{x},t')\mathrm{d}t'\right), \tag{2}$$

where $R_0^2=R^2(\mathbf{x}_0,t_0)$ and the subscript C means that the integral is evaluated along the trajectory $\mathbf{x}=\mathbf{x}(t)$ that at the time t_0 its position is $\mathbf{x}_0=\mathbf{x}(t_0)$.

The most important tool, for the purposes of the present work, is the so-called Bohm's total potential, defined as:

$$W(\mathbf{x}, t) = V(\mathbf{x}) + Q(\mathbf{x}, t) = V(\mathbf{x}) - \frac{h^2}{(8\pi^2 m)} \frac{\nabla_{\mathbf{x}}^2 R(\mathbf{x}, t)}{R(\mathbf{x}, t)}, \tag{3}$$

where the term denoted by $Q(\mathbf{x}, t)$ is known as Bohm's quantum potential. It is important to analyze this term in the context of the whole theory. If we substitute equation (2) into equation (1a) one obtains, after some rearrangement, Bohm's quantum potential as a function of the derivatives of $S(\mathbf{x}, t)$ with respect to the position. This leads to a new expression for the first quantum hydrodynamic equation

$$\frac{\partial S(\mathbf{x}, t)}{\partial t} + \frac{(\nabla_{\mathbf{x}} S(\mathbf{x}, t))^T (\nabla_{\mathbf{x}} S(\mathbf{x}, t))}{2m} - \frac{h^2}{(8\pi^2 m)} \left\{ \frac{1}{4m^2} \left[{}_C\int_{t_0}^{t} \nabla_{\mathbf{x}} (\nabla_{\mathbf{x}}^2 S(\mathbf{x}, t')) \mathrm{d}t' \right]^T \times \left[{}_C\int_{t_0}^{t} \nabla_{\mathbf{x}} (\nabla_{\mathbf{x}}^2 S(\mathbf{x}, t')) \mathrm{d}t' \right] - \frac{1}{2m} {}_C\int_{t_0}^{t} \nabla_{\mathbf{x}}^2 (\nabla_{\mathbf{x}}^2 S(\mathbf{x}, t')) \mathrm{d}t' \right\} + V(\mathbf{x}) = 0. \tag{4}$$

The integro-partial differential equation (4), along with the multiple-valued condition of the action function, namely $S'(\mathbf{x}, t) = S(\mathbf{x}, t) + nh$, being n an integer number, is equivalent to the TD Schrödinger equation.

According to equation (4), the quantum potential term $Q(\mathbf{x}, t)$ is, in fact, the shape of the local kinetic energy [11]. The importance of $Q(\mathbf{x}, t)$ stems on the fact that, thanks to (4), *quantum dynamics under $V(\mathbf{x})$, is totally equivalent to classical dynamics, even though trajectories have different total energies*. Whether or not the latter statement is relevant, is readily seen when one uses $Q(\mathbf{x}, t) + (\nabla_{\mathbf{x}} S(\mathbf{x}, t))^T (\nabla_{\mathbf{x}} S(\mathbf{x}, t))/(2m)$ to describe dynamical problems, like, e.g., a traveling WP colliding against a square barrier. From this point of view, the translation and "internal" motion of a WP is a result of the initial momentum given to the set of bohmian particles of the corresponding WP. In other words, the term $Q(\mathbf{x}, t) + (\nabla_{\mathbf{x}} S(\mathbf{x}, t))^T (\nabla_{\mathbf{x}} S(\mathbf{x}, t))/(2m)$, reflects the WP motion through the potential $V(\mathbf{x})$ [12].

The latter point of view, although completely correct, is computationally expensive if one wishes to get a global and comprehensive picture of the quantum dynamics, since it implies to evaluate a set of quantum trajectories. We may modify the situation by considering $W(\mathbf{x}, t)$, given in equation (3), as an effective total potential rather than a mix of external potential and a kinetic term. If we take this view then *quantum dynamics under $V(\mathbf{x})$, is totally equivalent to classical dynamics under the effective potential $W(\mathbf{x}, t)$*.

An example of this situation it is shown, for several time instances, in figure 2. Notice that we do not calculate trajectories, but only the effective total potential. For this problem, the classical total potential is zero outside the barrier, constant and positive inside it. On the other hand, the total potential

displays an inverted parabola shape in the region spanned by the WP, plus the squared shape from the classical potential. Contrary to $V(\mathbf{x})$, the total potential $W(\mathbf{x}, t)$ easily accounts for WP spreading. The potential felt by the traveling WP density, just an inverted parabola when it is far enough from the classical barrier, has a gradient changing sign across the WP maximum, accelerating the WP tails in opposite directions. Furthermore, as time progresses, the inverted parabola in $W(\mathbf{x}, t)$ widens, accounting for the well–known spreading slowdown as time increases. Note in passing that the traditional Schrödinger view does not provide a potential energy diagram that accounts for WP spreading, whereas Bohm's view is natural in this regard.

As stated, the dynamics associated to Schrödinger's probability density is classical, in terms of the effective total potential $W(\mathbf{x}, t)$. This feature may lead to an enhanced predictive capability, since the kinetic energy term preserves the classical structure, and due to this fact the qualitative dynamics may be extracted from the effective total potential shape. In other words, one may use $W(\mathbf{x}, t)$ diagrams in a manner parallel—but not identical, owing to W's time dependence—to the traditional classical potential energy diagrams are used. For instance, contrary to what happens with $V(\mathbf{x})$ in Schrödinger's view, a total potential barrier is a true barrier, in the sense that no particle may traverse it without having enough kinetic energy.

In addition, equations (1a) and (2) show that $W(\mathbf{x}, t)$ can be taken as a qualitatively correct indicator of quantum behavior. For instance, it is simply deduced from (1a) and (2) that the larger is the difference between $W(\mathbf{x}, t)$ and $V(\mathbf{x})$ (i.e., the larger is $Q(\mathbf{x}, t)$), the larger is the difference between classical and quantum dynamics. Inspection of figure 2, where in this case $N = 1$, clearly tells that when $W(\mathbf{x}, t)$ is getting closer to $V(\mathbf{x})$ as time progresses, then WP spreads. This is not surprising, for the definition of $Q(\mathbf{x}, t)$ shows that, for a given density or real positive amplitude, $R(\mathbf{x}, t)$, the quantum potential is smaller, more negative, the larger is the density curvature or real amplitude curvature, $\nabla^2_{\mathbf{x}} R(\mathbf{x}, t)$, at a given position. This an alternate form of stating that $Q(\mathbf{x}, t)$ depends on the density *shape*, rather than on the density *value* [8]. An immediate consequence of this latter statement is that, *as time progresses, the difference between quantum and classical dynamical behavior of a free WP changes*. At this point, one cannot neglect the possibility that, if a barrier is to be traversed, the quantum transmission might change depending on how much time the free WP has had to spread. This means that quantum transmission should depend on the distance traveled by the WP, between its launching and the ensuing collision.

The above effect has been inferred from qualitative arguments, thanks to the possibility of reasoning classically in terms of the TD effective potential $W(\mathbf{x}, t)$. However, these statements require a quantitative check. Given the lack of complete analytical solutions, for the WP transmission problem [13], it has

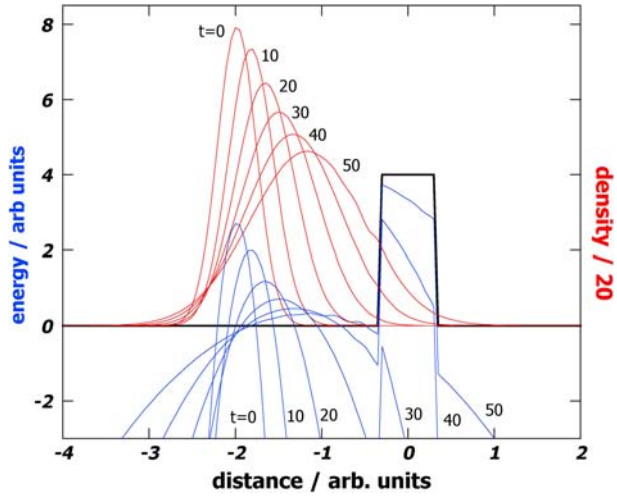

Figure 2. Time snapshots (from 0 to 50 a.u., in steps of 10), for a Gaussian WP colliding against a square barrier, $V_{\text{square barrier}}(\mathbf{x})$, and the corresponding effective potentials, $W(\mathbf{x}, t)$. Upper thin traces: TD wavefunction density. Upper thick trace: classical potential, $V(\mathbf{x})$ (square barrier). Lower thin traces: TD effective potential, $W(\mathbf{x}, t)$. Note that the effective potential, $W(\mathbf{x}, t)$, is the sum of an inverted parabola, $Q(\mathbf{x}, t)$ (Bohm's quantum potential), plus the square barrier, $V_{\text{square barrier}}(\mathbf{x})$. Whereas the square barrier is constant, the inverted parabola travels with the packet and opens as time progresses, yielding a slowdown of the density spreading. Note also that the classical barrier is absent in the effective potential, until the parabola is not wide enough. This happens later, the shorter is the launching distance.

to be performed numerically. Calculations have been performed, in the present case, using a TD Discrete Variable Representation (DVR) method. It is based on expanding the TD wavefunctions, in terms of stationary solutions of the complete problem, via a previous expansion of the latter in terms of sinc DVR basis functions [14]. The main advantage of this method is that it yields an especially simple matrix time-propagation algorithm, highly efficient for low-dimensional problems. The TD wavefunction is calculated from the expression:

$$\mathbf{y}(t) = \mathbf{L}^T \mathbf{t} \mathbf{L} \mathbf{j}_0, \tag{5}$$

where $\mathbf{y}(t)$ is the vector, of dimension M, containing the total wavefunction at each grid position, at time t, $\mathbf{t}$ is a diagonal matrix with diagonal elements, $\{exp(-iE_j t/\hbar)\}_{j=1}^{M}$, being, $\{E_j\}_{j=1}^{M}$, the set formed by the true eigensolutions of the *complete* problem (not plane wave energies), $\mathbf{L}$ is the eigenvectors matrix associated to the DVR–stationary basis change, whereas $\mathbf{j}_0$ is the vector corresponding to the initial WP, with components corresponding to its value at each grid position. The initial WP is chosen to be of gaussian, coherent-state form:

$$\varphi_0(x) = \left(\frac{2\sigma_0^2}{\pi}\right)^{1/4} \exp\left\{-\sigma_0^2(x - x_0)^2 + ip_0(x - x_0)\right\}, \tag{6}$$

where (x_0, p_0) establish the center of the packet, whereas σ_0 is a parameter related to the initial gaussian width.

3. Results and discussion

Figure 3 shows a case where two WPs, that have started to travel, at the same velocity or momentum, from different launching distances, are plotted at an instance they overlap the barrier. This instance, which is dependent on the initial WP position, has been set so that the total potential reaches the classical value, at the left edge of the square barrier. The corresponding total potentials are also shown. It is clear that $W(\mathbf{x}, t)$ for the second case is less negative, or more positive, than $W(\mathbf{x}, t)$ for the first WP, for the density fraction located on the barrier (and even in the close vicinity of it). Therefore, equivalent fractions of the packets experience different classical–like effective potential energies, $W(\mathbf{x}, t)$, leading to smaller classical-like kinetic energies, $(\nabla_{\mathbf{x}} S(\mathbf{x}, t))^T (\nabla_{\mathbf{x}} S(\mathbf{x}, t))/(2m)$, for the packet launched from a farther distance. It is important to notice that this behavior is linked to how much time the packet has been spreading.

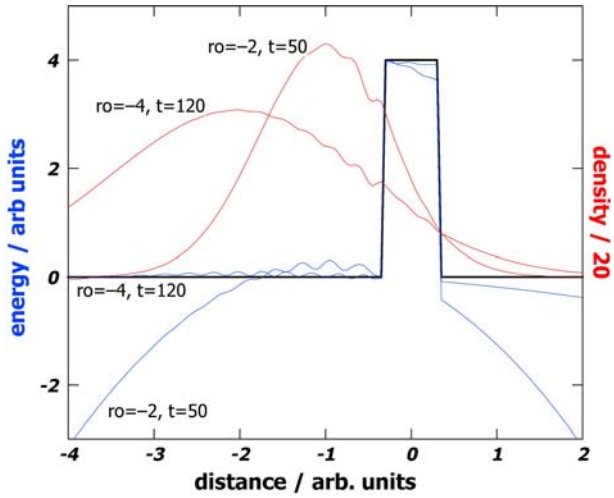

Figure 3. Two selected snapshots, for two WP that started at different distances from the square barrier. The snapshots correspond to the instance where the total potential reaches the classical value, for the left edge of the potential barrier. It may be evidenced, simply by visual inspection, that the transmitted area for the WP starting at $r_0 = -2$ is larger than the WP that started at $r_0 = -4$. This feature correlates with the more negative value of the total potential, the shorter is the time the WP has had to spread, before colliding against the potential barrier.

Hence one should conclude that the WP should lead to a smaller transmission, the larger is the launching distance.

This transmission factor has been calculated numerically, as a function of the initial launching distance. This factor, defined as the quotient between the transmitted and the incident areas, has been simply calculated as the transmitted area, for sufficiently large times, since the $t = 0$ WP has been normalized to unity. Calculations have been performed for a grid of mean WP energies, which cover a representative energy range, from the deep tunneling region and up to five times the barrier height.

Convergence has been a delicate issue in the present work. In particular, a careful, comprehensive check has been performed, to eliminate any dependence of the transmission factor on the grid spacing and size. Concerning the grid spacing, a typical feature in DVR-based methods, it has been found that above 200 points results change by less than one part in 10,000. On the other hand, table 1 shows results corresponding to the convergence test for the grid size, a delicate parameter since one has to avoid any finite size dependence, for the study of an open problem. Table 1 clearly shows that the grid dimensions do not

Table 1
Convergence test for the transmission factor, as a function of the grid size (L). The square barrier is placed at the mid-point of the grid, so that the launching distances (r_0) are measured after shifting the origin to the square barrier center. Horizontal axis stands for the mean WP energy, whereas the vertical axis includes several initial launching distances (r_0) and grid sizes (L).

	0.012	0.034	0.049	0.087	0.110	0.165
r_0=−1						
L=20	0.601179	0.850493	0.908145	9.6837E-01	9.8136E-01	9.9226E-01
L=25	0.601179	0.850510	0.908178	9.6846E-01	9.8156E-01	9.9239E-01
L=30	0.601179	0.850519	0.908198	9.6852E-01	9.8164E-01	9.9254E-01
L=35	0.601179	0.850520	0.908203	9.6854E-01	9.8168E-01	9.9259E-01
r_0=−2						
L=20	0.413662	0.797235	0.873554	9.5641E-01	9.7538E-01	9.9057E-01
L=25	0.413662	0.797252	0.873587	9.5649E-01	9.7550E-01	9.9071E-01
L=30	0.413662	0.797256	0.873599	9.5653E-01	9.8577E-01	9.9082E-01
L=35	0.413662	0.797256	0.873601	9.5654E-01	9.7559E-01	9.9085E-01
r_0=−3						
L=20	0.228515	0.715515	0.815485	9.3244E-01	9.6212E-01	9.8573E-01
L=25	0.228515	0.715528	0.815512	9.3251E-01	9.6223E-01	9.8589E-01
L=30	0.228515	0.715529	0.815518	9.3254E-01	9.6228E-01	9.8596E-01
L=35	0.228515	0.715529	0.815519	9.3255E-01	9.6230E-01	9.8597E-01
r_0=−4						
L=20	0.0994768	0.610829	0.733551	8.9179E-01	9.3745E-01	9.7428E-01
L=25	0.0994768	0.610836	0.733570	8.9185E-01	9.3755E-01	9.7440E-01
L=30	0.0994768	0.610836	0.733572	8.9187E-01	9.3758E-01	9.7444E-01
L=35	0.0994768	0.610837	0.733573	8.9186E-01	9.3759E-01	9.7444E-01

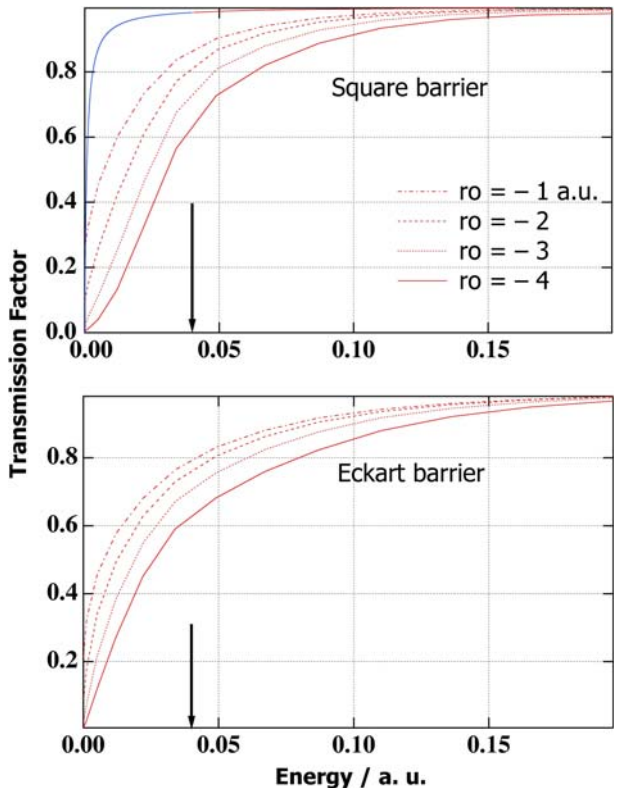

Figure 4. Transmission factor, as a function of the WP's mean energy, $p_0^2/2m$, for several initial launching distances, for the square and Eckart barrier problems. The classical potential barrier height has been set, in both cases, to $V = 0.04$ a.u., as indicated by the vertical arrow on the horizontal axis. The width of the square barrier was set to 0.05 a.u., whereas the mass of the traversing particle was set to $m = 367$ a.u. Distances are defined with respect to the center of the barrier, so that the WP collisions proceed from left to right. Note the upper trace, for the square barrier case, corresponding to the transmission factor, as a function of total energy, for a *stationary plane wave*.

have any influence in the numerical results, for the complete range of mean WP energies, as well as initial launching distances.

Figure 4 shows the results corresponding to converged calculations of the quantum transmission factor, for a coherent-state WP colliding against a square and an Eckart barrier. These results have arisen after a comprehensive exploration of masses, barrier widths and heights, as well as initial WP widths. It has been found that, the larger is the tunneling contribution to quantum transmission, the larger is also the dependence of transmission on the initial launching distance for a given energy. Figure 4 shows this effect, for a set of parameters, which make this dependence sufficiently large. Consequently, results show that the quantum transmission factor is dependent on the initial launching distance traveled by the packet, as a free WP. In particular, figure 4, square

barrier case, shows that the transmission factor is lower, the longer is the $t = 0$ particle–barrier distance. The same qualitative behavior is obtained for an Eckart barrier. It is obtained that transmission may vary up to 20% per Å, mainly in the tunneling region but also for energies well above the classical barrier height.

Whether or not the above feature is of general validity requires a further analysis. It is known that a WP, being a coherent state or not, being gaussian or not, always spreads as it travels, except for very few, specific cases. Consequently, it may be regarded spreading as a sufficiently general, key property. However, as the collision proceeds, the WP may strongly distort its original gaussian form, so that the spreading concept may turn senseless. A previous work [7] may be used to make this point much clearer. The authors studied several one-dimensional collision processes, by means of TDWP propagation. It turned out that the packet keeps most of its gaussian form up to well over the potential barrier.

A remarkable conclusion is then that a main source of quantum effects, in WP dynamics is the "spreading force," namely the presence of the inverted effective potential parabola, $W(\mathbf{x}, t)$, aligned to the WP, as shown in figure 2. This parabola is present in any kind of dynamical problem, as it arises solely from the own WP density or, in bohmian language, the ensemble distribution of bohmian particles with the corresponding momentum. In collision problems where the WP has time to spread before it collides, the total effective potential parabola, $W(\mathbf{x}, t)$, has time to reduce its curvature, becoming less negative. This behavior was described, in our previous work [7], in terms of WP sharpness: sharp WP profiles lead to a highly quantum particle, whereas smooth WP profiles lead to a more classical behavior.

It seems, therefore, a general result that quantum transmission, during the strong interaction between the particle and the barrier, is found to be more quantum the shorter is the time elapsed between the launching and the passage over the barrier. This conclusion might be used to complete a well-known analogy of WP motion [15], whereby spreading is pictured as the smearing shown by a traveling bunch of bullets, each having a different velocity. This image may be correct classically but, as shown in the present work, it lacks a fundamental quantum component. It is a purely quantum feature what is necessary to explain why the number of bullets actually traversing the barrier changes, as the width of the packet they define changes at the instance they get across the barrier.

It is possible to provide some quantitative relationships, in order to support the above statements. The fact that the inverted parabola shape is found to be the main component in the effective total potential, $W(\mathbf{x}, t)$, opens the possibility of using it to extract some physical insight. The time dependence of an effective potential, given by an inverted parabola of a propagation of a gaussian WP, is known analytically [9], being for $N = 1$:

$$W(x,t) = \frac{h^2}{(16\pi^2 m\sigma^2(t))}\left\{3 - \frac{(x-ut)^2}{2\sigma^2(t)}\right\}. \tag{7}$$

For a given time *t'*, the inverted parabola is centered at *ut'*, being *u* the translational velocity of the WP. Its second derivative, a measure of the curvature, is

$$\frac{\mathrm{d}^2 W(x,t)}{\mathrm{d}x^2} = -\frac{h^2}{(16\pi^2 m\sigma^2(t))} \tag{8}$$

so that its time dependence stems purely from the time dependence of σ, the gaussian width. It is given by:

$$\sigma(t) = \sigma_0\left\{1 + \left(\frac{ht}{(2\pi m\sigma_0^2)}\right)^2\right\}^{1/2} \tag{9}$$

with σ_0 the initial width at the initial time, $\sigma_0 = \sigma(t_0)$.

Equations (7)–(9) tell that the effective potential experiences a motion, which may be divided into two components. The first one reflects the drift, or rigid displacement of the whole WP, at a rate given by *u*, the central velocity of the packet. The second component is the opening of the inverted parabola, which is linked to the time variation of the gaussian width, and thus independent of the translational motion. The opening velocity of the effective potential may easily be accounted for from the rate of change of the gaussian width:

$$\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t} = \frac{ht}{(8\pi m^2\sigma(t)\sigma_0^2)} \tag{10}$$

thus being dependent on the mass of the particle, as well as on the initial and the current width.

This results show that one may tune the two components of the total potential separately, simply by acting on the translational velocity and initial spreading of the guiding WP, from the proper, for instance, inducting photons. One cannot avoid the conclusion that, for a given translational velocity and mass, one may enhance future quantum effects, in transmission processes, by tuning the initial gaussian width and/or selecting an adequate launching distance.

The present physical effect has been estimated to be of general validity, even though its intensity reduces with increasing barrier widths, masses, as well as collision energies. Hence it may be of experimental relevance. It is possible today to tame both light and matter WP, so as to control its initial shape and width to desired, accurate values, and thus provide the experimental conditions that maximize the presently reported effect.

In particular, results shown in figure 4 might correspond, concerning the reduced mass actually used, to a light particle (L) transfer between two heavy centers (H and H'), in, e.g., collinear triatomic reactions of the type H + LH' → HL + H'.

The transmission dependence on the initial launching distance might be sampled, to great accuracy, using femtosecond laser photoelectron spectroscopy, from stable anionic states pumped to neutral, rearrangement dissociative curves [16]. This analysis is supported by a simple quantitative estimation, from equation (10). For short times ($t \approx 1$ a.u.) and masses a fraction of a proton ($m \approx 400$ a.u., hence a typical HLH process) [17], one gets spreading rates of the order 0.25 Å/fs. This means that spreading may be tuned to be non-negligible, for distances and time scales typical of HLH molecular processes.

On another hand, electron transmission across solid conducting devices might also provide an adequate experimental framework for its detection, since deposition of nanoscopic oxide layers provide a kind of alteration in the solid electronic structure, which is frequently simulated by means of square classical potential energy barriers. Moreover, being an electron a lighter particle, the associated WP should display a sharper profile, enhancing, as it is well known, the intensity of quantum effects [18, 19]. The same quantitative estimation yields, for $m \approx 1$ a.u. (the mass of the electron) and short times, spreading velocities of ca. 500 nm/fs, thus being on the same scale than typical experimental processes.

Acknowledgments

J. G. gratefully thanks the CeRQT for providing a predoctoral fellowship. Financial support is acknowledged from the Spanish "Dirección General de Investigación (DGI)" and the "Fondo Europeo de Desarrollo Regional", through the grant CTQ2005-01117/BQU and from "Generalitat de Catalunya" grant 2005SGR-00111.

References

[1] H. Nakamura, *Non Adiabatic Transition* (World Scientific, Singapore, 2002).
[2] J.Z.H. Zhang, *Theory and Application of Quantum Molecular Dynamics* (World Scientific, Singapore, 1999).
[3] E.J. Heller, J. Phys. Chem. A 103 (1999) 10433.
[4] T.W. Wu, H.-J. Werner and U. Manthe, Science 306 (2004) 2227.
[5] R.T. Skodje and D.G. Truhlar, J. Chem. Phys. 80 (1984) 3123.
[6] J.G. Muga, S. Brouard and R.F. Snider, Phys. Rev. A 46 (1992) 6075.
[7] J. González, J.M. Bofill and X. Giménez, J. Chem. Phys. 120 (2004) 10961.
[8] A.S. Majumdar and D. Home, Phys. Lett. A 296 (2002) 176.
[9] P.R. Holland, *The Quantum Theory of Motion* (Cambridge University Press, Cambridge, 1993).
[10] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Wiley, New York, 1953).
[11] R.E. Wyatt, Chem. Phys. Lett. 313 (1999) 19.
[12] C.L. Lopreore and R.E. Wyatt, Phys. Rev. Lett. 82 (1999) 5190.
[13] Analytical solutions for the WP transmission problem are only available, from analytical solutions of the fixed-energy case, for the specific delta-function potentials studied in [6] (and references therein), or via the stationary phase approximation, for very large distances, orders of magnitude larger than those used in the present work.

[14] J.V. Lill, G.A. Parker and J.C. Light, Chem. Phys. Lett. 89 (1982) 89; D.T. Colbert and W.H. Miller, J. Chem. Phys. 96 (1992) 1982.
[15] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1980).
[16] M. Wollenhaupt, V. Engel and T. Baumert, Annu. Rev. Phys. Chem. 56 (2005) 25.
[17] A. Kuppermann, in: *Advances in Molecular Vibrations and Collision Dynamics*, ed. J.M. Bowman Vol. 2B (JAI Press, Greenwich, 1994) pp. 117–186.
[18] X. Oriols, F. Martín and J. Suñé, Sol. St. Commun. 99 (1996) 123.
[19] M. Bargheer, N. Zhavoronkov, Y. Gritsai, J.C. Woo, D.S. Kim, M. Woerner and T. Elsaesser, Science 306 (2004) 1771.