

# Simulation of quantum collinear chemical reactions with ultracold atoms

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Received 28 June 2011, in final form 15 August 2011

Published 13 September 2011

Online at [stacks.iop.org/JPhysB/44/195302](http://stacks.iop.org/JPhysB/44/195302)

## Abstract

We study a scaling and coordinate transformation to physically simulate quantum three-body collinear chemical reactions of the type  $A+BC \rightarrow AB+C$  by the motion of a single ultracold atom or a weakly interacting Bose–Einstein condensate on an L-shaped waveguide. We determine its feasibility with current technology and its limitations. As an example we work out the parameters to model the reaction  $F+H_2 \rightarrow H+HF$  by the propagation of ultracold lithium atoms.

## 1. Introduction

Ultracold atoms and ions are relatively easy to isolate, prepare, manipulate and detect by means of highly controllable operations that preserve their quantum coherence on the time scale of processes of interest. They have thus become natural candidates for performing physical, rather than numerical, simulations in which the effective Hamiltonians governing their dynamics can be made equal to the Hamiltonians of very different, simulated, quantum systems. These simulations are thus based on a formal analogy and could be potentially useful to predict the behaviour of the simulated system under conditions hard to realize and/or calculate in the original one, or because of a significant time gain over existing numerical computations. The simulating system may also be interesting on its own, beyond the parameters relevant for the simulation, and lead to genuinely new phenomena and applications [1]. This opens exciting perspectives for many-body physics [2], and also for few-body systems.

In this paper, we explore the analogy between reactive collinear three-body chemical reactions and the motion of a single cold atom, or possibly a weakly interacting Bose–Einstein condensate, on a potential surface designed by a magnetic or optical waveguide. Our interest, apart from setting the details of the mapping, is to determine its scope and limitations within state-of-the-art techniques. We put the

emphasis on the chemical reaction, but the same procedure may shed light also on non-reactive collisions. What we propose and what is facilitated by ultracold atoms is basically a quantum dynamical version of the well-known rolling ball analogy of chemical reactions [3, 4], with the ball ensemble substituted by a condensate or an ultracold-atom wavepacket, and the mechanical model potential by a magnetic or optical waveguide. Going beyond the classical model and having access to quantum effects is important for state-to-state (rather than averaged) results as well as for reactions involving a light-atom transfer such as hydrogen.

Most chemical reactions occur with steric requirements, i.e. a preferred direction of attack. The collinear configuration for the reaction path corresponds in many ‘abstraction’ reactions involving halogen and alkali atoms to the lowest potential barrier and to the preferred orientation within a narrow cone of acceptance [3]. Moreover collinear reactions may be induced by orienting cold polar molecules with strong electric fields via the second-order Stark effect [3]. They are also a standard workbench for testing new calculational methods, examining the range of validity of several approximate theories, and exploring parameter variations over a wide range of values, difficult to implement with full 3D calculations (the collinear configuration is mathematically reduced to a 2D problem). The results of interest are usually the branching ratios among the channels

or the distribution of produced molecules among the possible vibrational states. Even if time-dependent 2D Schrödinger equations are already solvable with current computers, the time reduction achievable by substituting the numerical computation by a physical simulation may be of several orders of magnitude. Our experience with time-dependent 2D propagations of a Rubidium condensate in a crossed-beam waveguide (a system that may exhibit classical chaos) is that an accurate calculation using a grid with  $10^9$  points, which is required to find quantum effects and agreement with experimental results, takes from several days to weeks in a super computer [5]. Compared to that, the physical propagation of the condensate along the waveguide takes milliseconds.

## 2. Simulation setting

The collinear chemical reaction  $A+BC \rightarrow AB+C$ , corresponds to the collision of an atom A and a nonrotating diatomic molecule BC with the three atoms aligned. We consider for simplicity distinguishable atoms to avoid quantum statistics, an unnecessary complication at this stage, and assume that the Born–Oppenheimer approximation holds so that the fast electronic and the slow nuclear motions can be separated. In terms of nuclear masses and positions and momenta in a laboratory frame, the nuclear motion is governed by the quantum-mechanical Hamiltonian:

$$H = \underbrace{\frac{p_A^2}{2m_A} + \frac{p_B^2}{2m_B} + \frac{p_C^2}{2m_C}}_{\mathcal{T}} + V(x_A, x_B, x_C), \quad (1)$$

where  $V$  is the effective interaction between the three nuclei. The first step is the transformation from ‘chemical reaction’ variables to atomic ‘simulation variables’. The second important task is to find out if the required parameters for the cold atom experiment are available with current technology.

### 2.1. Mass-weighted coordinate system

The use of mass-weighted coordinate systems to reduce the collinear reaction to a single effective particle moving on a 2D surface is well known [3]. Even so we shall provide the details to make clear the scaling options left for a simulation, in particular the possibilities of choosing the mass of the simulating atom, the timescale, and the consequences of the choices made on other variables whose values should be controlled.

Let us introduce the centre of mass (CM) coordinate  $R_{CM} := (m_A x_A + m_B x_B + m_C x_C)/M$ , where  $M := m_A + m_B + m_C$ , and the relative coordinates  $q_1 := x_B - x_A$ ,  $q_2 := x_C - x_B$ . Note that in the collinear case the atoms cannot cross, because of the infinite short distance repulsion, so these coordinates remain positive. The corresponding momentum operators are  $P_{CM} := \frac{\hbar}{i} \frac{\partial}{\partial R_{CM}} = p_A + p_B + p_C$ ,  $P_{q_1} := \frac{\hbar}{i} \frac{\partial}{\partial q_1} = \frac{m_A}{M} P_{CM} - p_A$ , and  $P_{q_2} := \frac{\hbar}{i} \frac{\partial}{\partial q_2} = p_C - \frac{m_C}{M} P_{CM}$ . The kinetic energy  $\mathcal{T}$  is

not diagonal in terms of them. To diagonalize  $\mathcal{T}$ , we use the mass-weighted coordinates [3]:

$$\begin{aligned} Q_1 &= (a q_1 + b q_2 \cos \beta) / (\sqrt{\tilde{m} l}), \\ Q_2 &= b q_2 \sin \beta / (\sqrt{\tilde{m} l}), \end{aligned} \quad (2)$$

with mass factors  $a = \sqrt{m_A(m_B + m_C)/M}$ ,  $b = \sqrt{m_C(m_B + m_A)/M}$ ,  $\tan \beta = \sqrt{m_B M / (m_A m_C)}$ , and scaling parameters  $\tilde{m}$  and  $l$  that we can choose freely. The corresponding momentum operators are

$$\begin{aligned} P_{Q_1} &:= \frac{\hbar}{i} \frac{\partial}{\partial Q_1} = \frac{la\sqrt{\tilde{m}}}{m_B + m_C} \left( -\frac{m_B + m_C}{m_A} p_A + p_B + p_C \right) \\ P_{Q_2} &:= \frac{\hbar}{i} \frac{\partial}{\partial Q_2} = bl \sin \beta \sqrt{\tilde{m}} \left( \frac{1}{m_C} p_C - \frac{1}{m_B} p_B \right), \end{aligned} \quad (3)$$

and the kinetic energy  $\mathcal{T}$  takes the form

$$\mathcal{T} = \frac{1}{2M} P_{CM}^2 + \frac{1}{2\tilde{m}l^2} (P_{Q_1}^2 + P_{Q_2}^2).$$

The connection between the simulation variables  $\{R_{CM}, Q_1, Q_2\}$  and the chemical reaction variables  $\{x_A, x_B, x_C\}$  is given by

$$\begin{aligned} x_A &= R_{CM} - \frac{al\sqrt{\tilde{m}}}{m_A} Q_1, \\ x_B &= R_{CM} + bl\sqrt{\tilde{m}} \left( \frac{\cos \beta}{m_C} Q_1 - \frac{\sin \beta}{m_B} Q_2 \right), \\ x_C &= R_{CM} + \frac{bl\sqrt{\tilde{m}}}{m_C} (\cos \beta Q_1 + \sin \beta Q_2). \end{aligned} \quad (4)$$

In the following, we ignore the trivial centre of mass motion and assume that the potential only depends on the relative differences between the particle positions. Then the corresponding time-dependent Schrödinger equation associated with the Hamiltonian (1) in the new variables is

$$i\hbar \frac{\partial \Psi}{\partial \tau} = -\frac{\hbar^2}{2\tilde{m}} \left( \frac{\partial^2}{\partial Q_1^2} + \frac{\partial^2}{\partial Q_2^2} \right) \Psi + V_Q(Q_1, Q_2) \Psi, \quad (5)$$

where we have set  $\tau = t/l^2$  and

$$V_Q(Q_1, Q_2) = l^2 V_q(q_1, q_2) = l^2 V(x_A, x_B, x_C). \quad (6)$$

Equation (5) is the important result to carry out the simulation, and describes 2D quantum motion of a quantum particle of mass  $\tilde{m}$  on the potential  $V_Q$ .

### 2.2. Potential energy surface

We now specify the potential surface  $V_q$  for the interaction between the three particles of the reaction. This might be an *ab initio* or, more generally, a semiempirical potential. Here we assume the semiempirical London–Eyring–Polanyi–Sato (LEPS) surface [6–8],

$$\begin{aligned} V_q(q_1, q_2) &= \frac{1}{1 + \Delta} \left[ \sum_{i=1}^3 U_i \right. \\ &\quad \left. - \sqrt{\sum_{i=1}^3 \alpha_i^2 - \alpha_1 \alpha_2 - \alpha_2 \alpha_3 - \alpha_1 \alpha_3} \right], \end{aligned} \quad (7)$$

where

$$U_i = \frac{1}{4} D_i [(3 + \Delta) e^{-2\beta_i(q_i - q_{i0})} - (2 + 6\Delta) e^{-\beta_i(q_i - q_{i0})}],$$

$$\alpha_i = \frac{1}{4} D_i [(1 + 3\Delta) e^{-2\beta_i(q_i - q_{i0})} - (6 + 2\Delta) e^{-\beta_i(q_i - q_{i0})}],$$

and  $q_3 = q_1 + q_2$ .  $D_i$ ,  $\beta_i$  and  $q_{i0}$  are the dissociation energy, the Morse parameter and the equilibrium distance of the *shape*  $i$ th diatomic molecules that we can construct from the three atoms. The adjustable parameter  $\Delta$  is optimized for each reaction. In the asymptotic regions, before and after the reaction happens, one of the atoms is far from the others and the potential energy is the one of a diatomic molecule [6]. In the LEPS surface, this is given by the Morse function:

$$V_j(q_j) = D_j [1 - e^{-\beta_j(q_j - q_{j0})}]^2, \quad (8)$$

where  $j = 1$  for the products' channel with the diatomic molecule AB, or  $j = 2$  for the reactants' channel with the diatomic molecule BC. This potential near the equilibrium distance  $q_{j0}$  can be harmonically approximated by

$$V_j(q_j) = \frac{1}{2} K_j (q_j - q_{j0})^2, \quad (9)$$

where  $K_j = 2D_j\beta_j^2$  is the force constant.

Applying equations (4) to the potential in the asymptotic regime where  $V_q(q_1, q_2) \approx V_j(q_j)$ , we obtain for the simulating frame that the energy surface in the asymptotic regions of the products' and reactants' channels are, taking equation (6) into account

$$V_Q(Q_1, Q_2) \approx \frac{1}{2} \tilde{K}_j [\chi_j(Q_1, Q_2) - \chi_{j,0}]^2, \quad (10)$$

where we have defined for the products' channel ( $j = 1$ )

$$\chi_{1,0} = q_{10} \frac{a \sin \beta}{l \sqrt{\tilde{m}}}, \quad \tilde{K}_1 = \frac{K_1 \tilde{m} l^4}{a^2 \sin^2 \beta},$$

$$\chi_1(Q_1, Q_2) = \sin \beta Q_1 - \cos \beta Q_2 = \frac{a \sin \beta}{l \sqrt{\tilde{m}}} q_1,$$

whereas for the reactants' channel ( $j = 2$ )

$$\chi_{2,0} = q_{20} \frac{b \sin \beta}{l \sqrt{\tilde{m}}}, \quad \tilde{K}_2 = \frac{K_2 \tilde{m} l^4}{b^2 \sin^2 \beta},$$

$$\chi_2(Q_1, Q_2) = Q_2 = \frac{b \sin \beta}{l \sqrt{\tilde{m}}} q_2.$$

The function  $\chi_1$  is a rotation in the  $(Q_1, Q_2)$  plane, so the potential (10) is, for the products, simply a rotated harmonic oscillator in the  $(Q_1, Q_2)$  plane. In terms of the oscillation frequencies of the diatomic molecules  $\nu_j$ , the frequencies  $\tilde{\nu}_j$  of the harmonic oscillators in equation (10) are

$$\tilde{\nu}_1 = \frac{l^2 \sqrt{\mu_{AB}}}{a \sin \beta} \nu_1, \quad \tilde{\nu}_2 = \frac{l^2 \sqrt{\mu_{BC}}}{b \sin \beta} \nu_2, \quad (11)$$

where  $\mu_{AB}$  and  $\mu_{BC}$  are reduced masses for the diatomic molecules. The value of  $l$  can be fixed from these last equations, to make the potential parameters of the simulation realistic.

### 2.3. Initial atomic velocity

To set the initial velocity of the cold atom  $v_{Q_1}$  in the reactants' channel we first estimate the velocities involved in the chemical reaction. If the reaction happens at temperature  $T$  the rms mean velocities for the atom A and diatomic molecule BC along a given direction are, respectively  $(k_B T / m_A)^{1/2}$  and  $[k_B T / (m_B + m_C)]^{1/2}$ , where  $k_B$  is the Boltzmann constant. We may then assume

$$v_C \approx v_B, \quad v_A - v_B = \sqrt{k_B T} \left( \frac{1}{\sqrt{m_A}} + \frac{1}{\sqrt{m_B + m_C}} \right), \quad (12)$$

which, from equations (3), corresponds to the simulating atom velocity

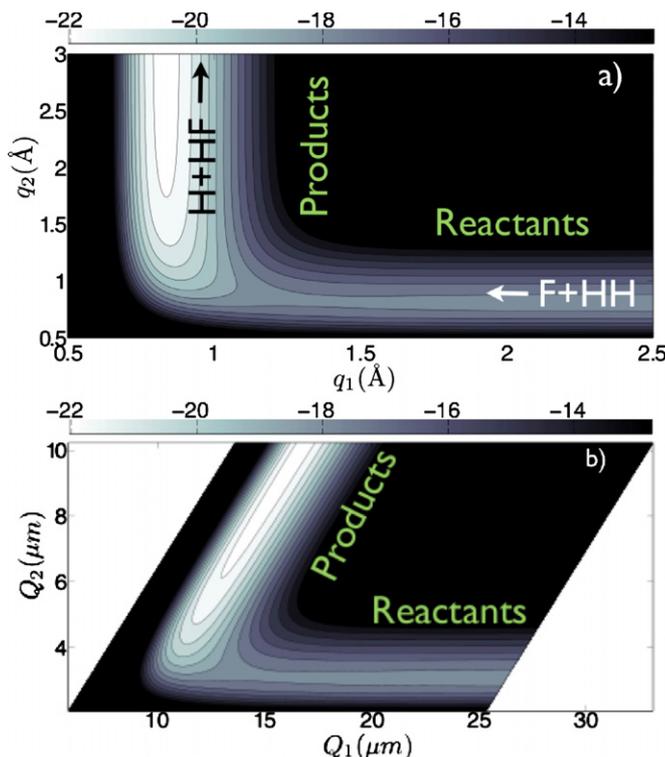
$$v_{Q_1} = \frac{la}{\sqrt{\tilde{m}}} (v_B - v_A) = al \sqrt{\frac{k_B T}{\tilde{m} m_A}} \left( 1 + \sqrt{\frac{m_A}{m_B + m_C}} \right), \quad (13)$$

$$v_{Q_2} \approx 0. \quad (14)$$

### 3. Example and numerical values

As an explicit example we consider the reaction  $F + H_2 \rightarrow FH + H$ , where  $F \rightarrow A$ ,  $H \rightarrow B$ , and  $H \rightarrow C$ , so  $m_A = 3.15 \times 10^{-26}$  kg and  $m_B = m_C = 1.66 \times 10^{-27}$  kg. For this particular reaction,  $\Delta = 0.164$  [7], and the mass factors are  $a = 5.48 \times 10^{-14}$ ,  $b = 3.98 \times 10^{-14}$  and  $\beta = 46.45^\circ$ . For the diatomic molecule HF,  $q_{10} = 0.917$  Å, the dissociation energy is  $D_1 = 9.609 \times 10^{-19}$  J and the Morse parameter  $\beta_1 = 2.242$  Å<sup>-1</sup>, so the force constant is  $K_1 = 2D_1\beta_1^2 = 966$  N m<sup>-1</sup>. Consequently the oscillation frequency  $\nu_1 = (K_1 / \mu_{HF})^{1/2} / 2\pi = 1.246 \times 10^{14}$  Hz, whereas for  $H_2$ ,  $q_{20} = 0.742$ ,  $D_2 = 7.608 \times 10^{-19}$  J,  $\beta_2 = 1.942$  Å<sup>-1</sup> and  $K_2 = 573.85$  N m<sup>-1</sup> so  $\nu_2 = (K_2 / \mu_{H_2})^{1/2} / 2\pi = 1.32 \times 10^{14}$  Hz.

To simulate the reaction we propose <sup>7</sup>Li atoms. One advantage of <sup>7</sup>Li is that the interatomic repulsive interactions are extremely tunable with a Feshbach resonance. The zero crossing of the *s*-wave scattering length is the shallowest known, so that only modest field stability is needed to achieve a non-interacting gas [9]. We thus have  $\tilde{m} = 1.1526 \times 10^{-26}$  kg and set  $l = 6.55 \times 10^{-6}$ . Defining the valley depths  $\tilde{V}_j = D_j l^2$  ( $j = 1, 2$ ) according to equation (6), the parameters in the asymptotic region for the reactants' channel are  $\tilde{\nu}_2 = 5.66$  kHz, and  $\tilde{V}_2 = 2.4$  μK, whereas in the asymptotic region of the products' channel,  $\tilde{\nu}_1 = 5.34$  kHz and  $\tilde{V}_1 = 3$  μK. The choice of a light atom such as lithium is also dictated by the requirement of achievable transverse frequencies in the reactants' and products' channels with standard techniques (see below). To illustrate the scaling of distances and velocities note that a displacement of 1 Å of the atom F along the reactants' channel corresponds to a displacement of 7.8 μm of the lithium atom according to equations (2). If the reaction occurs at room temperature,  $T = 298$  K, equation (13) sets for the lithium atom a velocity  $v_{Q_1} = 5$  mm s<sup>-1</sup> along the asymptotic region of the reactants' channel. The control of matter waves at such low velocities



**Figure 1.** (a) Contour map of the potential energy surface (7) for  $H_2 + F \rightarrow HF + H$ . (b) Contour map of the potential for the  ${}^7\text{Li}$  atom that simulates the chemical reaction. In both cases the energy is in units of the zero-point energy of the reactants' valley, and the surface is truncated well below zero energy (the asymptotic value when all atoms are far apart) to better visualize the saddle and reaction path.

(This figure is in colour only in the electronic version)

is at reach [10]. (For  $T = 12$  K,  $v_{Q_1} = 1$  mm s $^{-1}$  would still be feasible experimentally.) In figure 1 we plot the potential energy of the chemical reaction  $H_2 + F \rightarrow HF + H$  given by equation (7) to see the transformations from the chemical reaction parameters  $\{q_1, q_2\}$  into the 'laboratory' simulation waveguide on which the  ${}^7\text{Li}$  atom moves. Note the advanced saddle, and the deeper product's valley, responsible for the exoergicity and the vibrational excitation of the resulting HF molecule.

The experimental realization with ultracold atoms involves (i) the preparation of a propagating matter wave in a guide and (ii) the realization of a guide with the appropriate shape. A Bose–Einstein condensate, rather than the repetition of the experiment with single atoms, provides the ideal setting since the fate of the whole quantum wave packet can be measured in one single experiment. The propagation of a Bose–Einstein condensate into straight magnetic or optical guides has already been demonstrated experimentally [11, 12]. More recently, the production of guided atom lasers shows that a large control of the matter wave parameters such as the mean velocity (5–30 mm s $^{-1}$ ), the transverse mode occupations, the internal state, or the linear atomic density can be achieved [13–16]. Using different outcoupling mechanisms, the matter wave can be prepared in the transverse ground state [14, 15]. In these latter schemes, the diluteness of the matter wave suppresses the role of interactions providing a

well-suited system for the quantum scattering experiments of interest, without the need of Feshbach resonance tuning. The second aspect deals with the potential modelling to design simple reactive chemical reactions. Different strategies can be envisioned (i) with wires sculptured on atom chips by a focused atom beam technique [17, 18], (ii) with adiabatic radio-frequency potentials [19, 20], (iii) with high resolution time-averaged optical potentials 'painted' by a tightly focused rapidly moving laser beam on a 2D canvas formed by a static light sheet [21]. A canvas of 60  $\mu\text{m}$  diameter, and a radial condensate thickness of less than 1  $\mu\text{m}$  as the ones realized in [21], are enough for the spatial range and resolution needed for the simulation, see figure 1(b). Reaction probabilities could be detected with an *in situ* high-resolution imaging, whereas the coherent vibrational excitation is measurable after a few ms time-of-flight. High flexibility in the guide design is also provided by combining properly these various techniques and/or using time-dependent optical or magnetic potentials [22, 23]. A crude, simple realization would involve a crossed red-detuned dipole beams configuration in combination with a suitably positioned repulsive potential wall implemented by a sheet of blue-detuned laser light [24]. Playing with beam angles, waists, positions and intensities enables us to configure different standard features of the potential in the reaction region such as early and late barriers, or potential wells [24]. Alternatively, one could study the motion of an ion into a well-designed guide. Ultracold ions have already been transported in complex structures [25, 26], but their propagation in guides has not been investigated so far because of the damaging effect of heating mechanisms [27].

#### 4. Discussion and outlook

We have worked out the mapping between a quantum-mechanical collinear triatomic chemical reaction and the motion of ultracold atoms on a tilted, L-shaped waveguide. As an example we have got the parameters for simulating the reaction  $F + H_2 \rightarrow FH + H$  using  ${}^7\text{Li}$ , which can be implemented with currently available technology. This approach is thus complementary to other proposals for simulating chemical reactions [28], which are more *ab initio* and do not need any previous calculation of the potential surface or the Born–Oppenheimer approximation, but require a quantum computation with hundreds of coherently manipulated qubits. This is currently out of reach for a reaction like the one discussed. The present approach is less fundamental, since it assumes a potential surface and the Born–Oppenheimer approximation to hold, but also easier to implement.

By a straightforward generalization, we could also simulate collinear four-atom reactions with an ultra-cold atom moving on a three-dimensional potential. However, an obvious shortcoming of the mapping is the limitation to collinear configurations, which provide at best an approximation to the actual dynamics, mathematically 6D for a triatomic in the centre of mass, or 3D restricted to zero total angular momentum  $J = 0$ . Even if we could design a 3D interaction potential for the atomic motion, there is no

known transformation that allows the rolling ball analogy to be extended beyond the collinear case. For zero total angular momentum the kinetic energy of the triatomic system does not take the simple form, for known coordinate systems, of a particle moving on a potential surface. The closest result corresponds to a set of conformal Euclidean coordinates for which the kinetic energy reduces to the expected diagonal (cartesian, Laplacian) form, but with a position dependent prefactor [29]. Looking for physical systems that could realize this type of Hamiltonian is worthwhile.

The mentioned shortcoming imposes limits on possible applications. For example, the mapping could be the basis for an inverse scattering process to find an unknown potential making use of controlled potential changes and the time gain, but any disagreement with reaction experiments may be due to the limitation of the collinear model, instead of inaccuracies of the potential. The simulation must thus be discarded as an inversion tool of quantitative value.

Implementing physically actual collinear reactions would be possible in principle with ultracold atoms in waveguides. However, the one-atom simulation does not scale so as to mimic ultracold reactions with realistic parameters. As shown in the previous section, a room temperature reaction maps into a simulation in the ultracold regime. If the actual reaction temperature were already ultracold, the velocity of the simulating single atom would be far too low to be effectively controlled. Playing with the scaling factor  $l$  the velocity could be tuned to realistic values, but only at the price of producing unrealistic valley frequencies.

The proposed mapping provides in any case a useful pathway to transfer the vast knowledge and experience accumulated on chemical reaction dynamics, in particular for triatomic systems in the collinear configuration, into the design of crossed laser beams or waveguide bends with specific properties. These crossed beams or bent waveguides could be used, for example, as control devices for asymmetrical beam splitting into the different channels, or for controlling the transverse vibrational excitation. An example of this is the recent proposal of an atom diode or one-way barrier for atomic motion [24].

## Acknowledgments

We thank B Georgeot and C F Roos for discussions on this work. We acknowledge the kind hospitality of the Max Planck Institute for the Physics of Complex Systems in Dresden, and funding by the Basque Government (project no IT 472-10), Ministerio de Ciencia e Innovación (project no FIS2009-12773-C02-01), Région Midi-Pyrénées, Institut Universitaire de France and Agence Nationale de la Recherche (project no ANR-09- BLAN-0134-01). E T acknowledges support from the Basque Government (grant no BFI08.151).

## References

- [1] Gerritsma R, Kirchmair G, Zähringer F, Solano E, Baltt R and Roos C F 2010 *Nature* **463** 68
- [2] Bloch I, Dalibard J and Zwerger W 2008 *Rev. Mod. Phys.* **80** 885
- [3] Levine R D 2005 *Molecular Reaction Dynamics* (Cambridge: Cambridge University Press)
- [4] Fernández G M, Sordo J A and Sordo T L 1985 *J. Chem. Educ.* **62** 491
- [5] Gattobigio G L, Couvert A, Georgeot B and Guéry-Odelin D 2011 arXiv:1105.1971v1
- [6] Sato S 1955 *J. Chem. Phys.* **23** 592
- [7] Muckerman J T 1971 *J. Chem. Phys.* **54** 1155
- [8] Johnsons B R and Winter N W 1977 *J. Chem. Phys.* **66** 4116
- [9] Pollack S E, Dries D, Junker M, Chen Y P, Corcovilos T A and Hulet R G 2009 *Phys. Rev. Lett.* **102** 090402
- [10] Dries D, Pollack S E, Hitchcock J M and Hulet R G 2010 *Phys. Rev. A* **82** 033603
- [11] Bongs K, Burger S, Dettmer S, Hellweg D, Arlt J, Ertmer W and Sengstock K 2001 *Phys. Rev. A* **63** 031602
- [12] Leanhardt A E, Chikkatur A P, Kielpinski D, Shin Y, Gustavson T L, Ketterle W and Pritchard D E 2002 *Phys. Rev. Lett.* **89** 040401
- [13] Guerin W, Riou J F, Gaebler J P, Josse V, Bouyer P and Aspect A 2006 *Phys. Rev. Lett.* **97** 200402
- [14] Couvert A, Jeppesen M, Kawalec T, Reinaudi G, Mathevet R and Guéry-Odelin D 2008 *Europhys. Lett.* **83** 50001
- [15] Gattobigio G L, Couvert A, Jeppesen M, Mathevet R and Guéry-Odelin D 2009 *Phys. Rev. A* **80** 041605(R)
- [16] Kleine Büning G, Will J, Ertmer W, Klempt C and Arlt J 2010 *Appl. Phys. B* **100** 117
- [17] Reichel J 2002 *Appl. Phys. B* **74** 469
- [18] Della Pietra L, Aigner S, vom Hagen C, Groth S, Bar-Joseph I, Lezec H J and Schmiedmayer J 2007 *Phys. Rev. A* **75** 063604
- [19] Morizot O, Colombe Y, Lorent V, Perrin H and Garraway B M 2006 *Phys. Rev. A* **74** 023617
- [20] Lesanovsky I, Schumm T, Hofferberth S, Andersson L M, Krüger P and Schmiedmayer J 2006 *Phys. Rev. A* **73** 033619
- [21] Henderson K, Ryu C, MacCormick C and Boshier M G 2009 *New J. Phys.* **11** 043030
- [22] Madison K M, Chevy F, Wohlleben W and Dalibard J 2000 *Phys. Rev. Lett.* **84** 806
- [23] Kaplan A, Friedman N, Andersen M and Davidson N 2001 *Phys. Rev. Lett.* **87** 274101
- [24] Torrontegui E, Echanobe J, Ruschhaupt A, Guéry-Odelin D and Muga J G 2010 *Phys. Rev. A* **82** 043420
- [25] Blakestad R B, Ospelkaus C, VanDevender A P, Amini J M, Britton J, Leibfried D and Wineland D J 2009 *Phys. Rev. Lett.* **102** 153002
- [26] Singer K, Poschinger U, Murphy M, Ivanov P, Ziesel F, Calarco T and Schmidt-Kaler F 2010 *Rev. Mod. Phys.* **82** 2609
- [27] Roos C F 2011 private communication
- [28] Kassal I, Jordan S P, Love P J, Mohseni M and Aspuru-Guzik A 2008 *Proc. Nat. Acad. Sci.* **105** 18681
- [29] Katz G, Yamashita K, Zeiri Y and Kosloff R 2002 *J. Chem. Phys.* **116** 4403