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SKAGERSTAM and JOSÉ S. ANDRADE jr.

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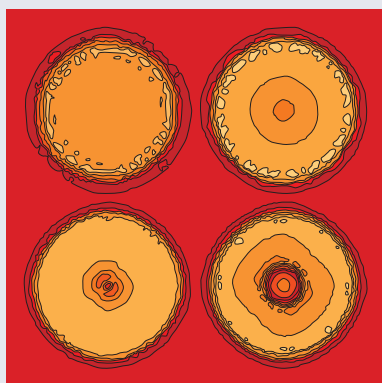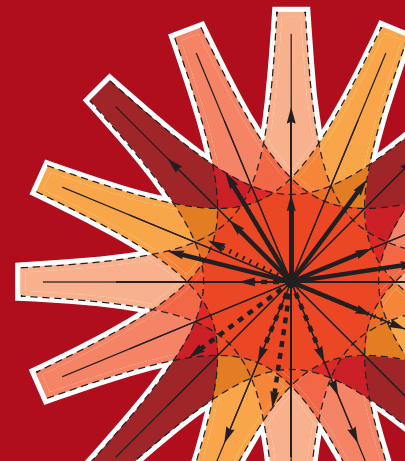European Physical Society   Società Italiana di Fisica   EDP Sciences   IOP Publishing
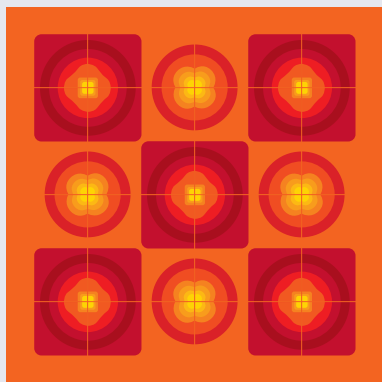
Morse potential derived from first principles

Raimundo N. Costa Filho[1(a)], Geová Alencar[2(b)], Bo-Sture Skagerstam[3,4(c)]
and José S. Andrade jr.[1(d)]

[1] *Departamento de Física, Universidade Federal do Ceará - Caixa Postal 6030, Campus do Pici,*
60455-760 Fortaleza, Ceará, Brazil
[2] *Faculdade de Educação, Ciências e Letras do Sertão Central, Universidade Estadual do Ceará*
R. Epitácio Pessoa, 2554, 63.900-000 Quixadá, Ceará, Brazil
[3] *Department of Physics, The Norwegian University of Science and Technology - N-7491 Trondheim, Norway*
[4] *Centre for Advanced Study (CAS) - Drammensveien 78, N-0271 Oslo, Norway*

Abstract – We show that a direct connection can be drawn, based on fundamental quantum principles, between the Morse potential, extensively used as an empirical description for the atomic interaction in diatomic molecules, and the harmonic potential. This is conceptually achieved here through a non-additive translation operator, whose action leads to a perfect equivalence between the quantum harmonic oscillator in deformed space and the quantum Morse oscillator in regular space. In this way, our theoretical approach provides a distinctive first-principle rationale for anharmonicity, therefore revealing a possible quantum origin for several related properties as, for example, the dissociation energy of diatomic molecules and the deformation of cubic metals.

The quantum harmonic oscillator (QHO) is certainly one of the most celebrated paradigms in quantum mechanics. Among its several important attributes, the QHO can be solved exactly and has been consistently used to approximate any potential function when Taylor expanded around their minima till second order. Moreover, the fact that bosons can be conceptually modeled in terms of a QHO readily explains its broad application, ranging from fundamental physics, in the description of a quantized electromagnetic field, to condensed matter, for vibrational properties of molecules as well as phonons in solids. However, anharmonic potentials are very often required to mathematically represent physical phenomena. For instance, an adequate description of the vibrational modes in diatomic molecules must necessarily allow for dissociation (*i.e.*, bond breaking) of its two bounded atomic nuclei. This essential feature is not compatible with the QHO model.

As originally proposed by Phillip M. Morse in 1929 [1], the so-called Morse potential provides a much better

description for the potential energy of a diatomic molecule than the QHO, being usually written as,

$$V_{\mathrm{M}}(r) = D(1 - e^{-\alpha r})^2, \qquad (1)$$

where r is the distance between atoms, D is the well depth related to the molecule dissociation energy, and α is an inverse length parameter related to the curvature of the potential at the origin. As such, this potential has been frequently used as an empirical model for anharmonic interactions in the study of a large variety of physical systems and conditions, including the rotating vibrational states of diatomic molecules [2], the adsorption of atoms and molecules by solid surfaces [3], and the deformation of cubic metals [4]. Figure 1 shows that, according to this potential, the energy difference between levels gradually decreases as the level number n increases.

Variants of the Morse potential have also been utilized to investigate the physical behavior of semiconductor surfaces and interfaces [5,6]. Also in the study of thermal denaturation of double-stranded DNA chains, the Morse potential has been successfully applied to model hydrogen bonds connecting two bases in a pair [7–10].

It is the purpose of this letter to show that the Morse potential emerges naturally as an effective interaction

[(a)]E-mail: rai@fisica.ufc.br
[(b)]E-mail: geova@fisica.ufc.br
[(c)]E-mail: bo-sture.skagerstam@ntnu.no
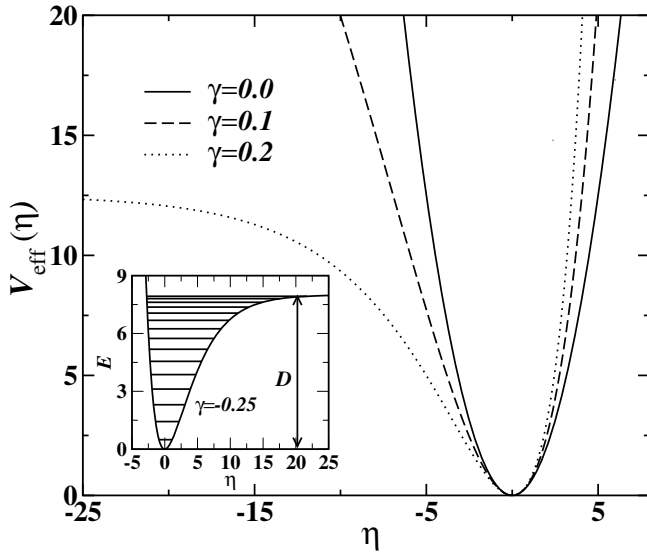[(d)]E-mail: soares@fisica.ufc.br

Fig. 1: The effective potential given by $V_{\text{eff}}(\eta) = D(1 - e^{\gamma\eta})^2$ for $\gamma = 0$ (solid line), $\gamma = 0.1$ (dashed line), and $\gamma = 0.2$ (dotted line). Here we use $\omega = 1$ and adopt atomic units, namely $\hbar = m = 1$. As shown, the anharmonicity of the potential depends on γ. The energy levels for $\gamma = -0.25$ are shown in the inset. The parameter D corresponds to the dissociation energy of the diatomic molecule.

when a particle is subjected to a harmonic potential in a contracted space. This physical situation is substantiated here in terms of the following quantum operator for non-additive translations [11,12]:

$$\langle x|U_\gamma(\varepsilon)|\psi\rangle = \psi(x + \varepsilon(1 + g(\gamma x))), \qquad (2)$$

where there is no restriction on $g(\gamma x)$. The action of $U_\gamma(\varepsilon)$ on the bra vector $\langle x|$ can therefore be expressed as $\langle x|U_\gamma(\varepsilon) = (U_\gamma(\varepsilon)^\dagger|x\rangle)^\dagger = \langle x + \varepsilon(1 + g(\gamma x))|$. For infinitesimal transformations we obtain that

$$U_\gamma(\delta x) = \mathbf{1} + \frac{i}{\hbar}\hat{p}_\gamma \delta x, \qquad (3)$$

and

$$\frac{i}{\hbar}\langle x|\hat{p}_\gamma|\psi\rangle = (1 + g(\gamma x))\frac{\mathrm{d}}{\mathrm{d}x}\langle x|\psi\rangle, \qquad (4)$$

where $\hat{p}_\gamma$ is the momentum operator. Considering the particular case where the function $g(\gamma x) = \gamma x$ and a finite displacement a, we can rewrite eq. (2) as

$$\langle x|U_\gamma(a)|\psi\rangle = \psi\left(xe^{\gamma a} + \frac{e^{\gamma a} - 1}{\gamma}\right), \qquad (5)$$

from which one can immediately recognize the action of the dilation/contraction operator $x\mathrm{d}/\mathrm{d}x$. It is worth mentioning that x has dimension of length and γ of the inverse of length. Moreover, as defined in eq. (2), the non-additive operator $U_\gamma(a)$ corresponds to the infinitesimal generator of the q-exponential function [13]

$$\exp_q(u) \equiv (1 + (1 - q)u)^{1/(1-q)}, \qquad (6)$$

where u is a dimensionless variable, and $\gamma \propto (1 - q)$. Equation (6) represents a fundamental mathematical definition for the generalized thermostatistics of Tsallis and its applications [14–21].

At this point, it is important to state that the momentum operator $\hat{p}_\gamma$ is Hermitian with regard to the following scalar product:

$$(\psi, \phi) = \int \frac{\mathrm{d}x}{1 + \gamma x}\psi^*(x)\phi(x), \qquad (7)$$

where the range of integration shall depend on the specific boundary conditions of the system under investigation. Equation (7) implies that the action of $U_\gamma(a)$ is unitary. Indeed, the measure of integration $\mathrm{d}x/(1 + \gamma x)$ is invariant under the action of the transformation, $x \to y = xe^{\gamma a} + (e^{\gamma a} - 1)/\gamma$, and the decomposition of the unit operator takes the form,

$$\mathbf{1} = \int \frac{\mathrm{d}x}{1 + \gamma x}|x\rangle\langle x|. \qquad (8)$$

The equation of motion for a particle in the x-representation of this dilated/contracted space corresponds to a time-dependent Schrödinger-like equation in the form,

$$i\hbar\frac{\partial}{\partial t}\psi(x, t) = H\psi(x, t), \qquad (9)$$

where the Hamiltonian operator is $H = \hat{p}_\gamma^2/2m + V(x)$, and the modified momentum operator can be written for short as $\hat{p}_\gamma = -i\hbar D_\gamma$, with $D_\gamma \equiv (1 + \gamma x)\mathrm{d}/\mathrm{d}x$ being a deformed derivative in space. Equation (9) can then be rewritten as

$$i\hbar\frac{\partial}{\partial t}\psi(x, t) = -\left(\frac{\hbar^2}{2m}\right)D_\gamma^2\psi(x, t) + V(x)\psi(x, t), \qquad (10)$$

or, more explicitly, as

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi(x, t) = &-(1 + \gamma x)^2\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x, t) \\ &-\gamma(1 + \gamma x)\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\psi(x, t) + V(x)\psi(x, t). \end{aligned} \qquad (11)$$

However, it is more convenient to express eq. (11) in terms of a simple change of variables, as suggested by the decomposition of the unit operator eq. (8). More precisely, we can define a variable η through the differential equation $\mathrm{d}\eta/\mathrm{d}x = 1/(1 + \gamma x)$ with boundary condition $\eta(0) = 0$, whose solution is

$$\eta = \frac{\ln(1 + \gamma x)}{\gamma}. \qquad (12)$$

From this transformation, it is important to notice that the "canonical coordinate" can be written as $x = (\exp(\gamma\eta) - 1)/\gamma$. In this way, a finite interval $[0, L]$ for x corresponds to $[0, \bar{L}]$, with $\bar{L} = \ln(1 + \gamma L)/\gamma$, for the

variable η. Equation (11) rewritten in terms of the new variable η becomes

$$i\hbar \frac{\partial}{\partial t}\phi(\eta,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\eta^2}\phi(\eta,t) + V_{\mathrm{eff}}(\eta)\phi(\eta,t), \qquad (13)$$

where $\phi(\eta,t) = \psi(x(\eta),t)$ and $V_{\mathrm{eff}}(\eta) = V(x(\eta))$. Assuming that

$$\phi(\eta,t) = \Phi(\eta)\exp\left(-iEt/\hbar\right), \qquad (14)$$

the transformation (12) leads us back to a more familiar version of the time-independent Schrödinger equation,

$$E\Phi(\eta) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}\eta^2}\Phi(\eta) + V_{\mathrm{eff}}(\eta)\Phi(\eta). \qquad (15)$$

If we now consider the problem of a standing wave in a null potential, $V_{\mathrm{eff}}(\eta) = 0$, it follows that the standard form of the plane wave solution is recovered in terms of the transformed variable η, namely $\Phi(\eta) = e^{\pm ik\eta}$. In the archetypal case of a harmonic oscillator, $V(x) = \frac{1}{2}m\omega^2 x^2$, the transformed effective potential becomes,

$$V_{\mathrm{eff}}(\eta) = \frac{m\omega^2}{2\gamma^2}(e^{\gamma\eta} - 1)^2, \qquad (16)$$

where ω is the frequency of the oscillator. Strikingly, by identifying $D \equiv m\omega^2/2\gamma^2$ and $\alpha \equiv -\gamma$, we conclude that eq. (16) corresponds exactly to the expression (1) for the Morse potential. To the best of our knowledge, this is the first time that a connection based on fundamental quantum principles is provided between this potential, which has been widely utilized as a consistent description for the vibrational structure of diatomic molecules, and the harmonic potential. A physical interpretation for this correspondence can be made in terms of a position-dependent (effective) mass induced due to the presence of a material body in the system [11] as, for example, the case of electrons propagating through abrupt interfaces in semiconductor heterostructures [22–26].

The wave function solution for the quantum Morse oscillator (QMO) has been previously determined as [1]

$$\Phi_n(z) = A_n z^s e^{-\frac{1}{2}z}L_n^{2s}(z), \qquad (17)$$

where $z = 2m\omega e^{\gamma\eta}/(\gamma^2\hbar)$, $s = m\omega/(\gamma^2\hbar) - n - 1/2$, $L_n^{2s}(z) = (z^{-2s}e^z/n!)\mathrm{d}^n(e^{-z}z^{n+2s})/\mathrm{d}z^n$ is the generalized Laguerre polynomial [27], and A_n is the normalization constant. The energies for the QMO can then be calculated as

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right)\left[1 - \frac{\gamma^2\hbar}{2m\omega}\left(n+\frac{1}{2}\right)\right], \qquad (18)$$

where the integer n is restricted by the condition $0 \leqslant 2n \leqslant 2m\omega/(\gamma^2\hbar) - 1$, leading to a finite number of bound states and $E_n \geqslant \hbar\omega(n+1/2)/2$. Equation (18) clearly indicates that, in the limit of small values of γ, the QHO spectrum is recovered. In the main plot of fig. 1 we show the form of the potential (16) for different values of γ, while in

the inset the energy levels are depicted for $\gamma = -0.25$. The potential is symmetric in γ, i.e., $V(\gamma) = V(-\gamma)$. The energy difference between levels decreases as the quantum number increases.

Finally, we show that an uncertainty relation for the QHO in the (deformed) x-representation can be disclosed in the framework of our theoretical approach. In order to do this, expected values for $\hat{x}$ and $\hat{p}$ must be calculated. Considering that the following correspondence holds between expected values of a given operator $\hat{O}$ in the x-space and η-space:

$$\left\langle \hat{O}_x \right\rangle_x = \left\langle \hat{O}_\eta \right\rangle_\eta = \int \mathrm{d}\eta\, \psi_n(\eta)^* O_\eta \psi_n(\eta), \qquad (19)$$

and using a procedure similar to the one adopted in ref. [28], we obtain,

$$\langle \hat{x} \rangle_{n,x} = -\frac{\gamma\hbar}{m\omega}\left(n+\frac{1}{2}\right), \qquad (20)$$

$$\langle \hat{p}_\gamma \rangle_{n,x} = 0, \qquad (21)$$

$$\langle \hat{x}^2 \rangle_{n,x} = \frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right), \qquad (22)$$

$$\langle \hat{p}_\gamma^2 \rangle_{n,x} = m\hbar\omega\left(n+\frac{1}{2}\right)\left[1 - \frac{\hbar\gamma^2}{m\omega}\left(n+\frac{1}{2}\right)\right], \qquad (23)$$

so that the uncertainty relation for the QHO in the (deformed) x-representation can be written as

$$\Delta x \Delta p_\gamma = \hbar\left(n+\frac{1}{2}\right)\left[1 - \frac{\gamma^2\hbar}{m\omega}\left(n+\frac{1}{2}\right)\right], \qquad (24)$$

which is always non-negative, as it should, due to the existence of a finite number of bound states. We attribute these remarkable features physically to the x-dependent effective mass previously alluded to.

For the ground state, eq. (24) is identical to the one previously obtained in ref. [11], namely $\Delta x \Delta p_\gamma \geqslant (\hbar/2)(1 + \gamma\langle x \rangle)$. The uncertainty of the QHO ground state in the (deformed) x-representation can therefore be smaller than the usual value $\hbar/2$. Note that in both expressions for energy (18) and uncertainty (24) the parameter γ, which defines whether the space is contracting ($\gamma < 0$) or dilating ($\gamma > 0$), appears squared. Consequently, for the harmonic potential in a deformed space, the energy is symmetric under contraction or dilation.

It is interesting to note that the Morse potential can be associated to a two-dimensional harmonic oscillator in polar coordinates for $\omega = 1$, and considering atomic units, $\hbar = m = 1$. In fact, it is this relationship that allows one to solve the QMO using ladder operators [29], and study this problem through supersymmetry [30]. As a consequence, our approach also provides a conceptual basis for the map between a 1D-QHO and a 2D-QHO in polar coordinates. This mapping is the result of the new commutation relation for $\hat{x}$ and $\hat{p}$ generated through the translation operator introduced in [11] and used here.

Previous studies have focused on plausible modifications on the position momentum [31–33], so that a minimum length and momentum could be defined for quantum theory. In particular, Quesne *et al.* [34] have shown that, if some special generalized deformed commutation relations are employed (*e.g.*, $[-e^{-x}, p] = i[e^{-x} + \beta p^2]$), the Morse potential can be obtained as an effective potential of the theory. In all these studies, however, modified commutation relations are introduced in an *ad hoc.* manner, *i.e.*, they are not obtained from a first-principle mechanism, like the non-additive translation operator employed in this work. Another important point here is that the parameter γ, responsible for the dilation/contraction in the translation, corresponds exactly to the minus value of the α parameter for the Morse potential. In the particular case of the Hydrogen molecule, for example, the numerical value of this parameter is $\gamma = -\alpha = -1.4$ a.u.

In summary, we have shown that a one-dimensional harmonic potential in a space deformed by the action of the operator defined as in eq. (2) can be equivalent to the Morse potential in a regular space. As the particle travels in a different way in the deformed space, it feels the harmonic potential as a Morse potential in regular space. This equivalence is achieved when $g(\gamma x) = \gamma x$, namely for the case in which the translation occurs as a contraction in a deformed space, $\gamma < 0$. Such a physical framework has perfect analogy with the behavior of a position-dependent (effective) mass particle on a non-homogeneous substrate, typified by electrons moving through abrupt interfaces in semiconductor heterostructures. In this particular situation, the anharmonic feature of the Morse potential emerges naturally from the standard quantum harmonic oscillator. We should point that the transformation used here is very similar to the one used in general relativity, where there the position x transforms to a function $f(x)$, in opposition to a Galilean transformation that is additive. We thus conclude that our study, based on a non-additive translation operator, provides a first-principle explanation for anharmonic properties.

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