

Comments on *Morse Potential Derived From First Principles* by Filho Raimundo et al

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1 Summary

$$V_M(x) = D(1 - e^{-\alpha x})^2 \quad (1)$$

$$D = \text{well depth} \quad (2)$$

$$\alpha = \text{an inverse parameter related to the curvature of the potential} \quad (3)$$

Figure 1: The Morse Potential

The quantum harmonic oscillator (QHO) is a simple model that approximated the vibrational bond nodes by considering the interaction as oscillations between two atoms. However, the problem with using a spring to approximate the energy of a diatomic molecule was that a simple spring did not allow dissociation to occur. Philip Morse was able to account for this mathematically by creating the equation in Figure 1 above that effectively described the potential of a diatomic molecule. However this model was strictly a mathematical solution. By utilizing Tsallis thermostatics, Raimundo et al[1] show that the Morse potential is a natural consequence of applying the Shrodinger equation to a simple translation of two particles bound to each other.

$$\begin{aligned} U_\gamma(a)|x > &= x + a + a(g(\gamma x)) = x + a(1 + g(\gamma x)) \\ &= x + a(1 + \gamma x), \quad g(\gamma x) = \gamma x \end{aligned} \quad (4)$$

$$S(A + B) = S(A) + S(B) + (1 - \gamma)S(A + B) \quad (5)$$

Figure 2: Applying Nonadditive Entropy to the Defined Translation Operator stepsize a

While a simple translation operator would be additive, Raimundo et al introduce a new function $g(\gamma(x))$ based on *nonextensive thermostatics*. In essence, Dr. Constantino Tsallis had postulated that at a quantum scale, entropy is no longer additive, and introduces an influence of γ into the system. As the scale of interaction grows, so does the γ factor, which reverts to the additive form of entropy that is familiar. Figure 3 shows the influence of γ on entropy. If entropy is influenced by proximity, then there must be some function $g(\gamma x)$ that influences the translation of the system at the quantum scale. Because the focus is on deriving the Morse potential, the paper assigns the function to be γx for further derivations.

$$U_\gamma(\delta x) = 1 + \frac{i}{\hbar} p_\gamma \delta x \quad (6)$$

$$= |x + \delta x(1 + \gamma x) > \quad (7)$$

$$\therefore p_\gamma |x > = -i\hbar(1 + \gamma x) \frac{\partial}{\partial x} |x > \quad (8)$$

Figure 3: Deriving the Momentum Operator, p_γ from Applying Quantum Definitions to Simple Translation

The translation operator applies a deviation that depends on the momentum to the identity of the initial vector space defined. By applying an infinitesimal deviation with the translation operator to the simple spacial function x , it can be seen that the momentum operator can be derived from the translation operator.

$$\begin{aligned} H|\psi(x, t) > &= i\hbar \frac{\partial}{\partial t} \psi(x, t) \\ &= \frac{p_\gamma^2}{2m} \psi(x, t) + V(x) \psi(x, t) \\ &= E\psi(x, t) \end{aligned} \quad (9)$$

Figure 4: Shrodinger Equation and the Hamiltonion Operator

By knowing the form of the momentum operator, the time independant Shrodinger Equation shown in Figure 4 can be used to solve for the energy of the quantum system.

$$\begin{aligned} H|\psi(x, t) > &= \frac{p_\gamma^2}{2m} \psi(x, t) + V(x) \psi(x, t) \\ &= -\frac{\hbar^2}{2m} (1 + \gamma x) \frac{\partial^2}{\partial x^2} \psi(x, t) + V(x) \psi(x, t) \end{aligned} \quad (10)$$

$$= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \eta^2} \phi(x, t) + V_{eff}(\eta) \phi(\eta, t) \quad (11)$$

$$\eta = \frac{\ln(1 + \gamma x)}{\gamma} \rightarrow x = \frac{\exp(\gamma \eta) - 1}{\gamma} \quad (12)$$

Figure 5: Applying the Defined Momentum Operator to the Shrodinger Equations

Figure 5 shows the outcome of applying the momentum operator found in Figure 2 to the Shrodinger equation. At first glance it seems that the introduction of γ has complicated the system. But by defining a canonical coordinate, $\eta(x)$, Raimundo et al show that the equation returns to a form familiar to the previously defined Hamiltonian, which can be solved for a simple two particle system. By applying the canonical coordinate to the potential for a quantum harmonic oscillator where $V(x) = \frac{1}{2}m\omega^2 x^2$, the Morse potential emerges as shown in Figure 6.

$$V_M(x) = D(1 - e^{-\alpha x})^2 \quad (13)$$

$$= \frac{m\omega^2}{2\gamma^2}(e^{\gamma\eta} - 1)^2$$

$$E_M = (v + 0.5)v_e - (v + 0.5)^2 v_e x_e + (v + 0.5)^3 v_e y_e + \dots \quad (14)$$

Figure 6: The Morse Potential Derived from First Principles with Improvements and the Associated Energy Equation

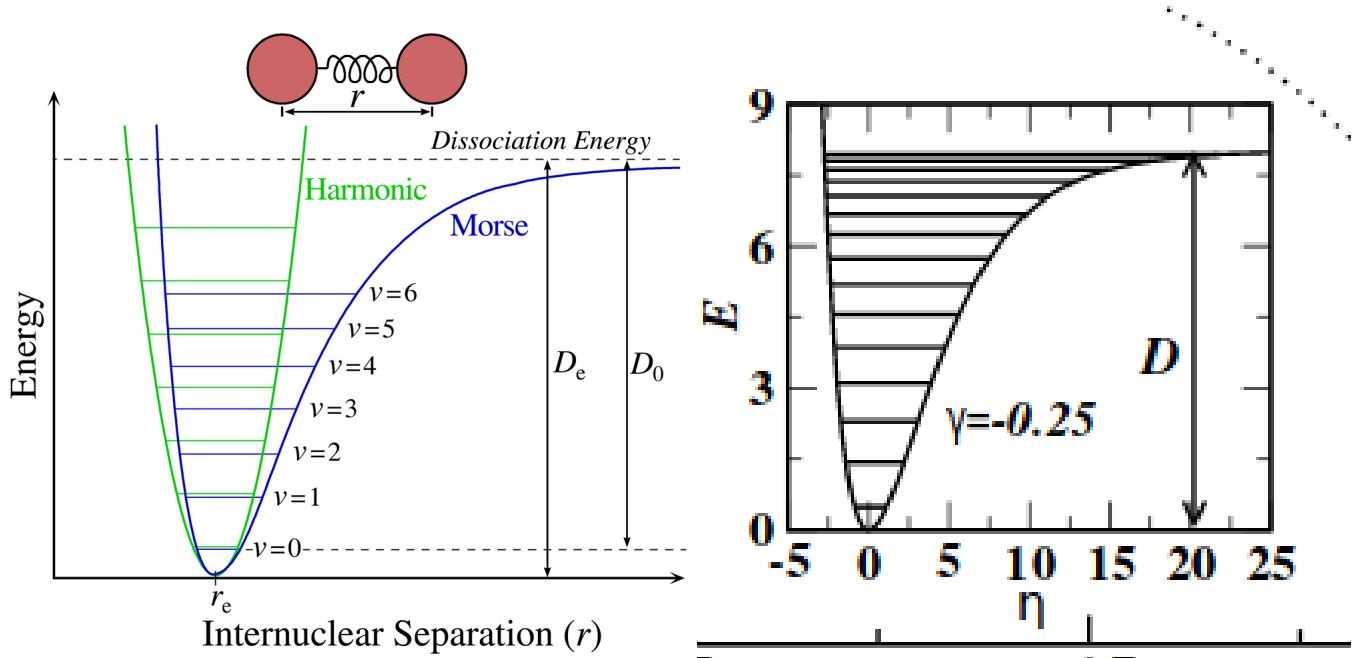


Figure 7: Comparison of the Morse Potential Derived Mathematically (left) and Physically (Right)

Comparison of the two variants of the Morse potential mathematically and visually show strong similarity between the two. However, the potential that Raimundo et al derive can be seen visually that it better approximates the energy of a system between than the mathematical model. Figure 7 shows the comparison of the two plots. It can be seen that while the both show the appearance of discrete energy levels, the derivation model's energy levels do not have equally spaced discrete energy levels, which is closer to molecular systems in reality. This is a product of introducing the Tsallis entropy. As the particles grow farther apart, γ increases such that the increase in entropy as energy increases is decreasing. This results in the decreases in spacing between energy levels for the system. Though the derivation does not hold for systems that contain more than two particles, it is still strong nonetheless showing two strong characteristics: particles will dissociate provided enough energy and spacing between discrete energy levels decrease as the quantum number (that defines vibrational modes of the system), v , grows. Furthermore, a key point to note is that the momentum operator was found by using a simple x function, and not with the commonly used wavefunction $\psi(x, t)$. This implies the strength of the QHO; simple translation of a particle bound to another can be used to describe a complex wavefunction that describes the oscillations of two particles. By knowing the potential energy of the system, the total energy equation can be determined as well, fully solving the Shrodinger equation.

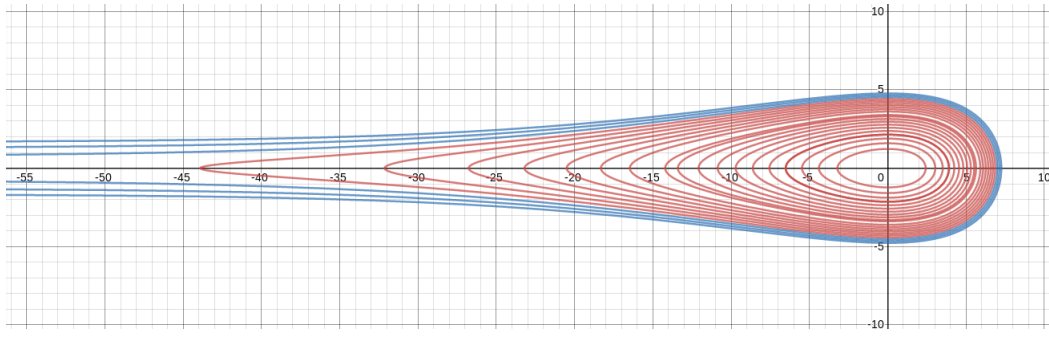


Figure 8: Bifurcation Diagram based on Derived Energy and Potential from Figure 6

A bifurcation diagram can be made using $x' = \sqrt{2(E_M - V_M(x))}$, which is effectively a top-down view of the well defined in Figure 7. The red denotes the stable limits cycles, and the blue denotes when the limit cycle is broken and no longer stable. As the quantum number grows, so do the size of the cycles i.e. the length of oscillation increases as energy increases. At a certain energy level, bifurcation occurs where the limit cycles are no longer stable, signifying dissociation between the two particles. The blue instability is confirmed by intuitive understanding that once the two particles have dissociated, there would be no oscillation between the two. The bifurcation parameters that define the Morse potential can be confirmed by simple physical intuitions. *Desmos* was used to manipulate the bifurcation parameters. As shown by the rising well, it can be easily seen that v is one bifurcation parameters. m, γ also control bifurcation as well. For a spring, as the mass of the particles that are connected increase, the energy decreases. The same thought can be applied here where increasing the mass of the system delays bifurcation. Entropy is indirectly tied to the γ factor. From basic Gibbs-free energy, as entropy increases, the overall energy decreases. This is the same as decreasing the γ factor (which would increase the overall entropy; refer to Figure 3), which would deepen the potential well and delay bifurcation.

2 Afterword

The lecture on energy curves was what sparked my inspiration for choosing this paper. I had difficulty understanding the "philosophy" of the course, but this piece was very effective in tying together ODE observations made in class to how they emerge in PDE systems of interest. I also would like to thank my partner Guhnveer Bahia for his help because had he not been there, I would not have been able to tie together my chemical and mathematical knowledge to this physical phenomenon. The presentation was a good opportunity for me to conclude my learning and go further with Dirac notation and operator theory, and I enjoyed it regardless of the crunch from my schedule.

References

- [1] R. N. C. Filho, G. Alencar, B.-S. Skagerstam, and J. S. A. Jr. Morse potential derived from first principles. *Europhysics Letters*, 101(1):1 – 4, 2013.