

Kinetic Energy Is Important in the Nanoscale World

Frank Rioux

Department of Chemistry
College of St. Benedict & St. John's University
St. Joseph, MN 56374

Most explanations of atomic and molecular phenomena found in textbooks are expressed in terms of potential-energy-only (PEO) models. Inclusion of kinetic energy in the analysis is generally considered to be unnecessary or irrelevant. This view is of questionable validity, and it is becoming increasingly clear that ignoring kinetic energy at the nanoscopic level can lead to facile but incorrect explanations of atomic and molecular behavior. (1-4)

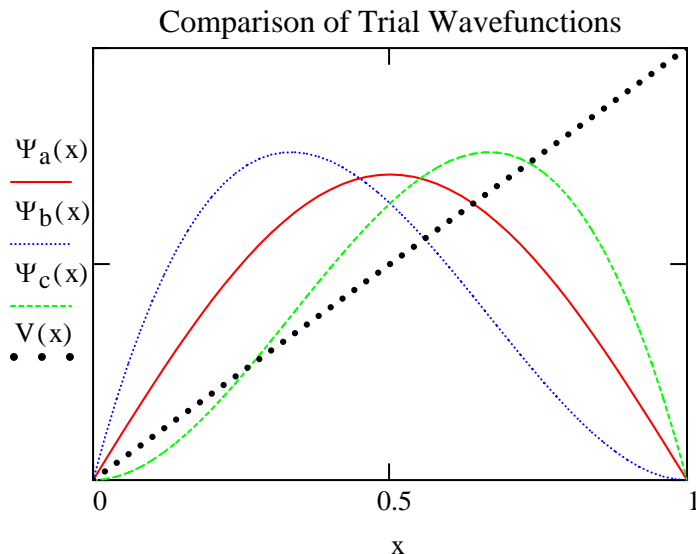
The idea that kinetic energy should not be ignored is not too surprising since quantum mechanical calculations involve minimization of the total energy, which includes both kinetic and potential energy contributions. In other words, kinetic energy plays an important role at the computational level, and therefore should not be excluded at the level of analysis and interpretation. For example, the fundamental questions regarding the stability of matter, the nature of the covalent bond, and the interaction of electromagnetic radiation with matter cannot be answered without a consideration of kinetic energy in the quantum mechanical context. (5)

The following simple variational calculation on a particle in a one-dimensional box with a linear internal potential clearly illustrates the importance of kinetic energy. For a particle of unit mass in a one-dimensional box of length one bohr ($1a_0 = 52.9 \text{ pm} = 0.0529 \text{ nm}$) with internal potential energy $V = 2x$ the Schrödinger equation in atomic units ($\hbar = 2\pi$) is,

$$\frac{-1}{2} \cdot \frac{d^2}{dx^2} \Psi(x) + V(x) \cdot \Psi(x) = E \cdot \Psi(x) \quad \text{where} \quad V(x) := 2 \cdot x$$

Three normalized trial wave functions are considered in this analysis, and are shown below both mathematically and graphically. The potential energy function is superimposed on the graphical representation of the trial wave functions.

$$\Psi_a(x) := \sqrt{2} \cdot \sin(\pi \cdot x) \quad \Psi_b(x) := \sqrt{105} \cdot x \cdot (1-x)^2 \quad \Psi_c(x) := \sqrt{105} \cdot x^2 \cdot (1-x) \quad x := 0, .02.. 1$$



If asked to choose the best trial wave function by inspection, one would undoubtedly be inclined to select Ψ_b because it is skewed to the left side of the box where the potential energy is lowest. Ψ_a would be next best because it is symmetric, and Ψ_c would be last because it is skewed to the right side of the box where the potential energy is highest. However, the quantum mechanical calculations reveal that Ψ_a is the best trial function of the three because it gives the lowest total energy, the primary criterion of the variational principle.

For each trial wave function the expectation values for kinetic energy (T), potential energy (V), total energy ($E = T + V$), and position are calculated. Atomic units are used all calculations: $1E_h = 4.36 \text{ aJ}$ and $1a_0 = 52.9 \text{ pm}$)

Calculations for trial wave function Ψ_a

$$\text{Kinetic energy: } T_a := \int_0^1 \Psi_a(x) \cdot -\frac{1}{2} \cdot \frac{d^2}{dx^2} \Psi_a(x) dx \quad T_a = 4.935$$

$$\text{Potential energy: } V_a := \int_0^1 \Psi_a(x) \cdot 2 \cdot x \cdot \Psi_a(x) dx \quad V_a = 1.000$$

$$\text{Total energy: } E_a := T_a + V_a \quad E_a = 5.935$$

$$\text{Average position: } X_a := \int_0^1 \Psi_a(x) \cdot x \cdot \Psi_a(x) dx \quad X_a = 0.500$$

Calculations for trial wave function Ψ_b

$$\text{Kinetic energy: } T_b := \int_0^1 \Psi_b(x) \cdot -\frac{1}{2} \cdot \frac{d^2}{dx^2} \Psi_b(x) dx \quad T_b = 7.000$$

$$\text{Potential energy: } V_b := \int_0^1 \Psi_b(x) \cdot 2 \cdot x \cdot \Psi_b(x) dx \quad V_b = 0.750$$

$$\text{Total energy: } E_b := T_b + V_b \quad E_b = 7.750$$

$$\text{Average position: } X_b := \int_0^1 \Psi_b(x) \cdot x \cdot \Psi_b(x) dx \quad X_b = 0.375$$

Calculations for trial wave function Ψ_c

$$\text{Kinetic energy: } T_c := \int_0^1 \Psi_c(x) \cdot -\frac{1}{2} \cdot \frac{d^2}{dx^2} \Psi_c(x) dx \quad T_c = 7.000$$

$$\text{Potential energy: } V_c := \int_0^1 \Psi_c(x) \cdot 2 \cdot x \cdot \Psi_c(x) dx \quad V_c = 1.250$$

$$\text{Total energy: } E_c := T_c + V_c \quad E_c = 8.250$$

$$\text{Average position: } X_c := \int_0^1 \Psi_c(x) \cdot x \cdot \Psi_c(x) dx \quad X_c = 0.625$$

These calculations are summarized in following table.

Property\Wave function	Qa	Qb	Qc
Kinetic Energy/ E_h	4.935	7.000	7.000
Potential Energy/ E_h	1.000	0.750	1.250
Total Energy/ E_h	5.935	7.750	8.250
Average Position/ a_0	0.500	0.375	0.625

Ψ_a is a symmetric function which favors neither the low potential energy region nor the high potential energy region, but has the lowest total energy because it has a significantly lower kinetic energy than the other trial wave functions. The reason it has a lower kinetic energy is because it has a lower curvature than the other wave functions (curvature is the second derivative of the function). Ψ_b has a somewhat lower potential energy than Ψ_a because it favors the left side of the box, but consequentially a much higher kinetic energy because of its greater curvature. Total energy, as noted above, is what counts in a variational calculation. Ψ_c is the worst trial function because it has both high kinetic energy and high potential energy.

Of course, Ψ_a is not the best possible wave function for this problem; it is only the best of the three considered here. The best wave function can be found by a more elaborate variational calculation or by numerical integration of Schrödinger's equation. A Mathcad (6) program for numerical integration of Schrödinger's equation for a particle in a box with linear internal potential is given in the appendix.

This latter method yields a wave function with the following physical properties: $\langle T \rangle = 4.942 E_h$; $\langle V \rangle = 0.983 E_h$; $\langle E \rangle = 5.925 E_h$; $\langle X \rangle = 0.491 a_0$. Note that this optimum wave function is skewed a little to the left of center, increasing kinetic energy slightly (+.007 E_h) and reducing potential energy slightly more (-.017 E_h), and overall yielding an energy reduction of -.01 E_h . The details of these calculations can be found in the appendix.

However, it is also important to note that Ψ_a , the eigenfunction for the particle in a box problem [$V(x)=0$], is a very good trial wave function for this particular problem. It is in error by only 0.17% when compared with the more accurate, and essentially exact, numerical solution. Ψ_a is displayed along with the numerical wave function in the appendix to show how little it differs from the numerical solution.

Another point that should be noted is that Ψ_b does not become the preferred trial function until $V(x) = 16.6x$. In other words it requires a rather steeply rising internal potential energy to offset the kinetic energy advantage that Ψ_a has. The energy calculations for both wave functions are given below.

$$V_a := \int_0^1 \Psi_a(x) \cdot 16.6 \cdot x \cdot \Psi_a(x) dx \quad V_a = 8.300 \quad E_a := T_a + V_a \quad E_a = 13.235$$

$$V_b := \int_0^1 \Psi_b(x) \cdot 16.6 \cdot x \cdot \Psi_b(x) dx \quad V_b = 6.225 \quad E_b := T_b + V_b \quad E_b = 13.225$$

In conclusion, this simple example reveals that our intuition about the importance of potential energy in the analysis of physical phenomena at the nanoscale level should be tempered by a realization that the quantum mechanical nature of kinetic energy cannot be safely ignored.

Literature cited:

1. Tokiwa, H.; Ichikawa, H. *Int. J. Quantum Chem.* **1994**, *50*, 109-112.
2. Rioux, F.; DeKock, R. L. *J. Chem. Educ.* **1998**, *75*, 537-539.
3. Weinhold, F. *Nature* **2001**, *411*, 539-541.
4. Rioux, F. *Chem. Educator* **2003**, *8*, S1430-4171(03)01650-9; DOI 10.1333/s00897030650a..
5. In the context of quantum mechanics, confinement energy is probably a better descriptor than kinetic energy, because the latter implies classical motion. According to quantum mechanical principles, confined particles, because of their wave-like character, are described by a weighted superposition of the allowed position eigenstates. They are not executing a trajectory in the classical sense. In other words, they are not here and later there; they are here and there, simultaneously.
6. Mathcad 11 is a product of Mathsoft, Cambridge, MA 02142; <http://www.mathsoft.com/>.

Appendix

Numerical Solution for the Particle in a Slanted Box

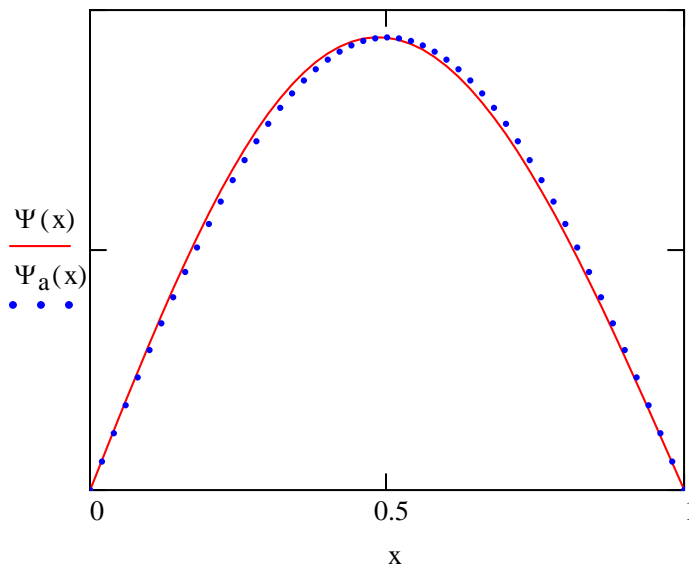
Parameters: $x_{\max} := 1$ $m := 1$ $V_0 := 2$ Potential energy: $V(x) := V_0 \cdot x$

Solve Schrödinger's equation numerically:

Given $\frac{-1}{2 \cdot m} \cdot \frac{d^2}{dx^2} \Psi(x) + V(x) \cdot \Psi(x) = E \cdot \Psi(x) \quad \Psi(0) = 0 \quad \Psi'(0) = 0.1$

$\Psi := \text{Odesolve}(x, x_{\max})$ Normalize wavefunction: $\Psi(x) := \frac{\Psi(x)}{\sqrt{\int_0^{x_{\max}} \Psi(x)^2 dx}}$

Enter energy guess: $E \equiv 5.925$



Calculate most probable position: $x := .5$ Given $\frac{d}{dx} \Psi(x) = 0$ Find(x) = 0.485

Calculate average position: $X_{\text{avg}} := \int_0^1 \Psi(x) \cdot x \cdot \Psi(x) dx \quad X_{\text{avg}} = 0.491$

Calculate potential and kinetic energy: $V_{\text{avg}} := V_0 \cdot X_{\text{avg}} \quad V_{\text{avg}} = 0.983$

$T_{\text{avg}} := E - V_{\text{avg}} \quad T_{\text{avg}} = 4.942$