Theory of Moment Propagation for Quantum Dynamics in Single-Particle Description

Nicholas Boyer, Christopher Shepard, Ruiyi Zhou, Jianhang Xu, and Yosuke Kanai
Dept. of Chemistry, University of North Carolina at Chapel Hill
Dept. of Physics and Astronomy, University of North Carolina at Chapel Hill

Introduction and Motivation

Recent development of real-time time-dependent density functional theory (RT-TDDFT) in maximally-localized Wannier functions (MLWF) gauge and the use of the artificial neural network (ANN) for modeling quantum dynamics have motivated us to explore how single-particle time-dependent Schrodinger equation can be reformulated as the dynamics of moments of the position operator. A theoretical formalism for this moment propagation is developed and numerical demonstrations are given for simple proof-of-principle systems where analytical solutions can be derived. We further propose how ANN can be used to perform efficient quantum dynamics simulations with the newly developed moment propagation theory.

Moments of the position operator are given by

$$\langle x^a y^b z^c \rangle (t) = \int\int\int x^a y^b z^c n(x,y,z,t)\,dxdydz$$

Time-dependent Schrodinger equation (TDSE):

$$i\frac{\partial \psi(x,y,z,t)}{\partial t} = -\frac{1}{2}\nabla^2\psi(x,y,z,t) + V(x,y,z,t)\psi(x,y,z,t)$$

Theoretical Formulation

$$\frac{\partial < x^a y^b z^c > (t)}{\partial t} = \int\int\int x^a y^b z^c \dot{n}(x,y,z,t)\,dxdydz$$
$$= -i\int\int\int \Big(a x^{a-1} y^b z^c \frac{\partial \psi}{\partial x}\psi^* + \frac{a(a-1)}{2} x^{a-2} y^b z^c n(x,y,z,t)$$
$$+ b y^{b-1} x^a z^c \frac{\partial \psi}{\partial y}\psi^* + \frac{b(b-1)}{2} y^{b-2} x^a z^c n(x,y,z,t) + c z^{c-1} x^a y^b \frac{\partial \psi}{\partial z}\psi^*$$
$$+ \frac{c(c-1)}{2} z^{c-2} x^a y^b n(x,y,z,t)\Big)\,dxdydz$$

$$\frac{\partial^2 < x^a y^b z^c > (t)}{\partial t^2} = Re\Big(-\int\int\int (a x^{a-1} y^b z^c \frac{\partial V(x,y,z,t)}{\partial x} n(x,y,z,t)$$
$$+ b x^a y^{b-1} z^c \frac{\partial V(x,y,z,t)}{\partial y} n(x,y,z,t) + c x^a y^b z^{c-1} \frac{\partial V(x,y,z,t)}{\partial z} n(x,y,z,t))\,dxdydz$$
$$- \int\int\int (a(a-1) x^{a-2} y^b z^c \frac{\partial^2 \psi}{\partial x^2}\psi^* + 2ba x^{a-1} y^{b-1} z^c \frac{\partial^2 \psi}{\partial x \partial y}\psi^*$$
$$+ 2ca x^{a-1} y^b z^{c-1} \frac{\partial^2 \psi}{\partial x \partial z}\psi^* + b(b-1) y^{b-2} x^a z^c \frac{\partial^2 \psi}{\partial y^2}\psi^*$$
$$+ 2cb y^{b-1} x^a z^{c-1} \frac{\partial^2 \psi}{\partial y \partial z}\psi^* + c(c-1) z^{c-2} x^a y^b \frac{\partial^2 \psi}{\partial z^2}\psi^*)\,dxdydz$$
$$+ a(a-1)(\frac{(a-2)(a-3)}{4} < x^{a-4} y^b z^c > + \frac{b(b-1)}{2} < y^{b-2} x^{a-2} z^c >$$
$$+ \frac{c(c-1)}{2} < z^{c-2} x^{a-2} y^b >) + b(b-1)(\frac{(b-2)(b-3)}{4} < y^{b-4} x^a z^c >$$
$$+ \frac{c(c-1)}{2} < z^{c-2} x^a y^{b-2} >) + \frac{c(c-1)(c-2)(c-3)}{4} < z^{c-4} x^a y^b >\Big)$$

Moments and wave function

$$\psi(x,y,z,t) = \sqrt{n(x,y,z,t)}\,e^{i\theta(x,y,z,t)}$$

The particle density, *n*, can be obtained from the moments via Edgeworth series [1]. Here the 1D case is demonstrated.

$$n(x) = \frac{pdf(\frac{x-\kappa_1}{\sigma})}{\sigma}$$

$$pdf_n(x) = z(x)(1 + \sum_{j=1}^{n-2}(\sum_{\{P_{j_m}\}}^{\{P_j\}}(\prod_{i=1}^{\infty}\frac{1}{k_i!}(\frac{\lambda_{i+2}}{(i+2)!})^{k_i})He_s(x)))$$

where $\{P_j\}$ is the set of all positive integer partitions of j. An integer partition of integer j is all the possible ways to sum up positive integers to j. For example, if j = 3, then the integer partitions are 1 + 1 + 1 =1 + 2 = 3. For each partition P_{jm} within P_j, where m is the index of the partition in the set:

$$\sigma = \sqrt{\kappa_2} \qquad k_i = P_{j_m}.count(i)$$
$$\lambda_n = \frac{\kappa_n}{\sigma^n} \qquad s = j + 2\sum_{i=1}^{\infty} k_i$$

$$He_n(x) = n!\sum_{j=0}^{\lfloor \frac{n}{2} \rfloor}\frac{(-1)^j x^{n-2j}}{2^j (n-2j)! j!} \qquad \kappa_a = \mu_a - \sum_{i=1}^{a-1}\binom{a-1}{i-1}\kappa_i \mu_{a-i}$$
$$z(x) = \frac{1}{\sqrt{2\pi}}\exp(\frac{-(x)^2}{2})$$

Derivatives of the phase can be expressed as

$$\frac{d\theta(x,y,z,t)}{dx} = (-n(x,y,z,t))^{-1}\int_{-\infty}^{x}\alpha_x(u,y,z,t)\,du$$

$$\alpha_x = \sum \frac{dn}{d < x^a >}\frac{d < x^a >}{dt} + \sum c_x^{ab}\frac{dn}{d < x^a y^b >}\frac{d < x^a y^b >}{dt}$$
$$+ \sum c_x^{ac}\frac{dn}{d < x^a z^c >}\frac{d < x^a z^c >}{dt} + \sum c_x^{abc}\frac{dn}{d < x^a y^b z^c >}\frac{d < x^a y^b z^c >}{dt}$$

$$c_x^{abc}\frac{d < x^a y^b z^c >}{dt} = \int\int\int x^a y^b z^c \alpha_x\,dxdydz \qquad \dot{n} = \alpha_x + \alpha_y + \alpha_z$$

In practice, the numerical difference quotient can be used with the Edgeworth series to calculate α_x.

[1] S. Blinnikov and R. Moessner, "Expansions for nearly gaussian distributions", Astronomy and Astrophysics Supplement Series 130, 193–205 (1998)

Moment Propagation Equation of Motion

The explicit wave function dependence for the second time-derivative is removed to yield the equation of motion for the moment propagation theory (MPT).

$$c_x^{abc}\frac{\partial^2 < x^a y^b z^c > (t)}{\partial t^2} = -\int\int\int (a x^{a-1} y^b z^c \frac{\partial V(x,y,z,t)}{\partial x} n(x,y,z,t))\,dxdydz$$
$$+ \int\int\int (a(a-1) x^{a-2} y^b z^c (\frac{(\frac{dn(x,y,z,t)}{dx}^2)}{4n(x,y,z,t)} + \frac{L_x(x,y,z,t)^2}{n(x,y,z,t)})$$
$$+ ba x^{a-1} y^{b-1} z^c (\frac{(\frac{dn(x,y,z,t)}{dx}\frac{dn(x,y,z,t)}{dy})}{4n(x,y,z,t)} + \frac{L_x(x,y,z,t)L_y(x,y,z,t)}{n(x,y,z,t)})$$
$$+ ca x^{a-1} y^b z^{c-1} (\frac{(\frac{dn(x,y,z,t)}{dx}\frac{dn(x,y,z,t)}{dz})}{4n(x,y,z,t)} + \frac{L_x(x,y,z,t)L_z(x,y,z,t)}{n(x,y,z,t)}))\,dxdydz$$
$$- a(a-1)(\frac{(a-2)(a-3)}{4} < x^{a-4} y^b z^c > + \frac{b(b-1)}{4} < y^{b-2} x^{a-2} z^c > + \frac{c(c-1)}{4} < z^{c-2} x^{a-2} y^b >)$$

$$L_x(x,y,z,t) \equiv -\int_{-\infty}^{x}\alpha_x(u,y,z,t)\,du$$

Electron Potential Energy Surface (EPES)

When the energy conservation principle holds, the second time derivative can be also found using

$$< \ddot{x}_k > = -\frac{dE(< x_i >, < \dot{x}_i >)}{d < x_k >}\frac{< \dot{x}_k >}{\frac{dE(< x_i >, < \dot{x}_i >)}{d < \dot{x}_k >}}$$

Analytical Solution for Harmonic Potential w/ Homogeneous E-Field

For $V(x)=x^2 + c(t)x$, the analytical solution can be obtained

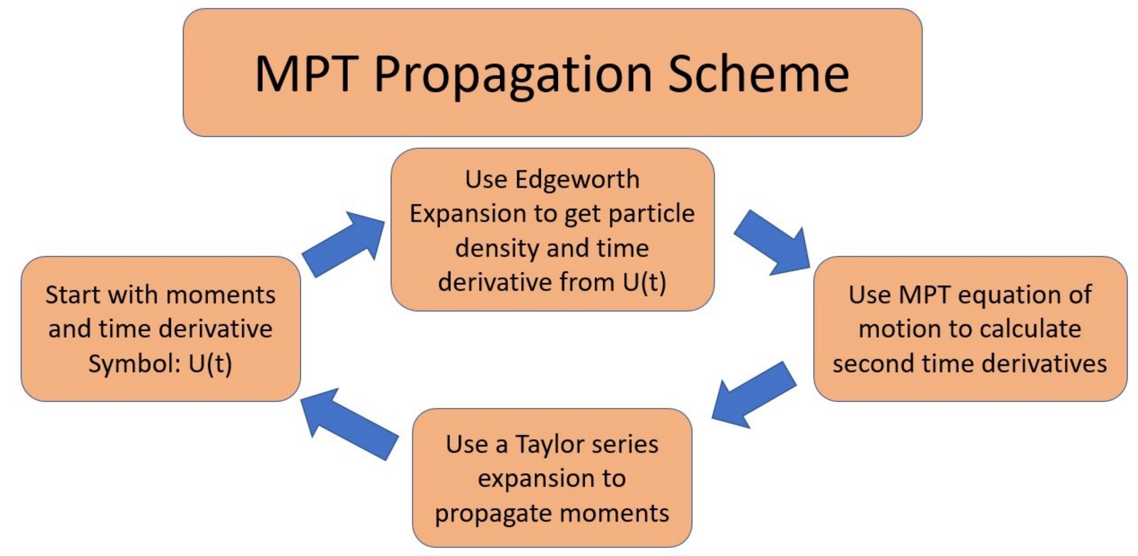
$$\frac{d^2 < x >}{dt^2} = -2 < x > - c(t)$$

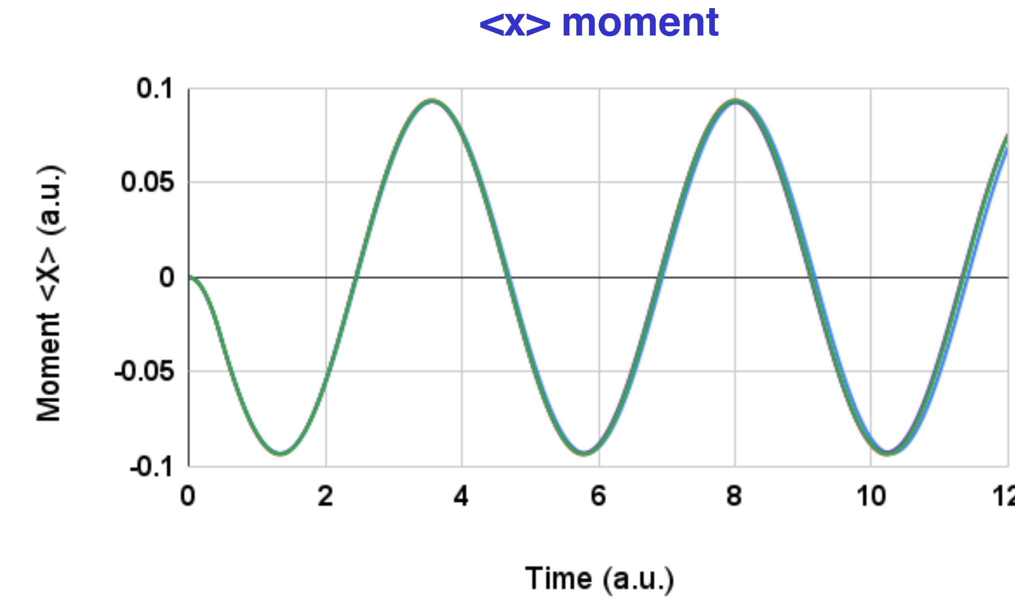
$$\frac{d^2 < x^2 >}{dt^2} = -4 < x^2 > - 2c(t) < x > + 2((\frac{d < x >}{dt})^2 + \frac{1 + (\frac{dS}{dt})^2}{4S})$$

$S = <x^2> - <x>^2$

$$E = < x^2 > + c(t) < x > + 0.5((\frac{d < x >}{dt})^2 + \frac{1 + (\frac{dS}{dt})^2}{4S})$$

Numerical Demonstration

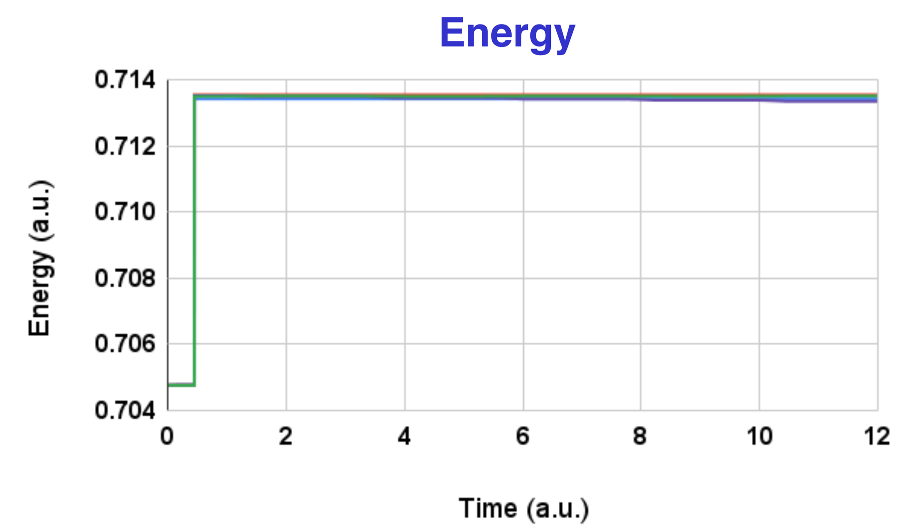


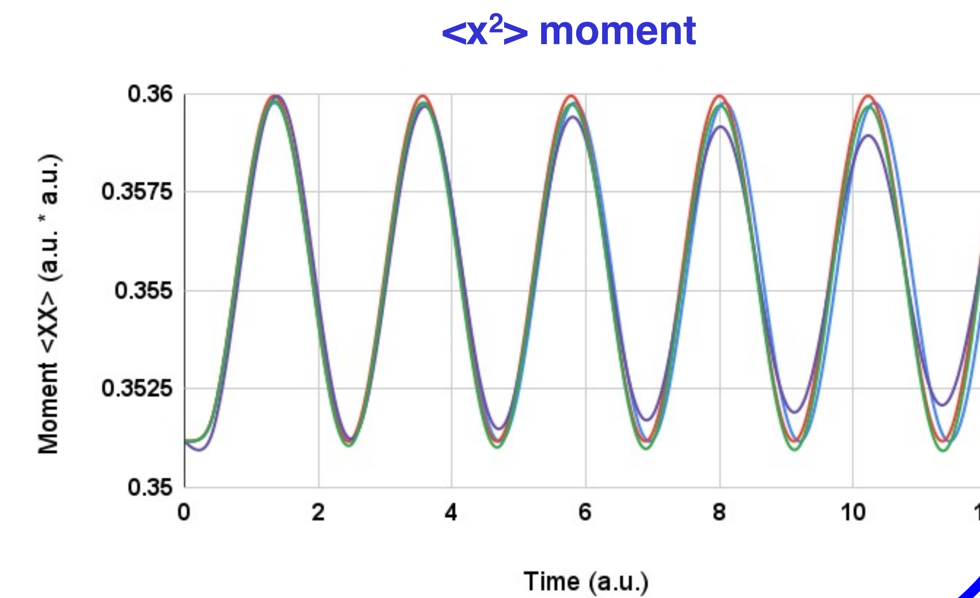


1D harmonic potential with external electric field given by

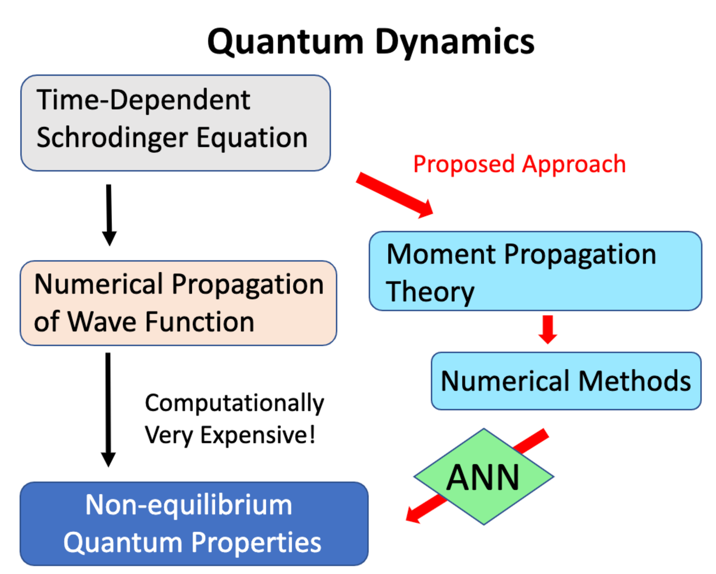
$$c(t) = \begin{cases} 0.3 & \text{if } t < 0.45 \\ 0 & \text{if } t \geq 0.45 \end{cases}$$

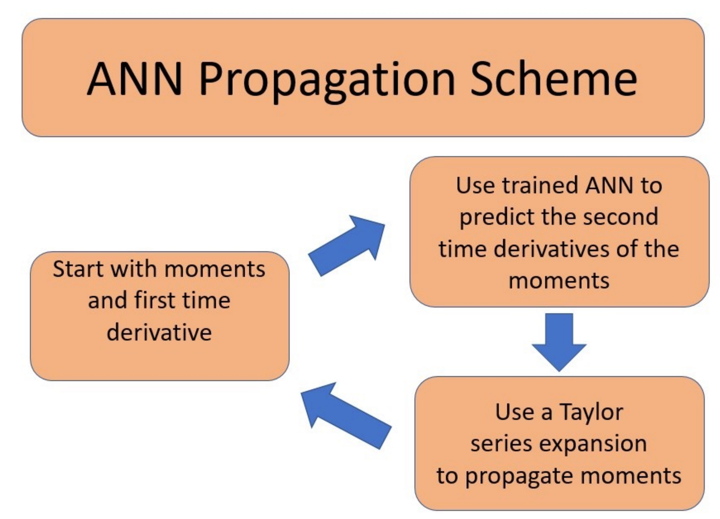
Wave function propagation (TDSE)
MPT w/ 2nd-order Edgeworth
MPT w/ 4th-order Edgeworth
EPES w/ 2nd-order Edgeworth

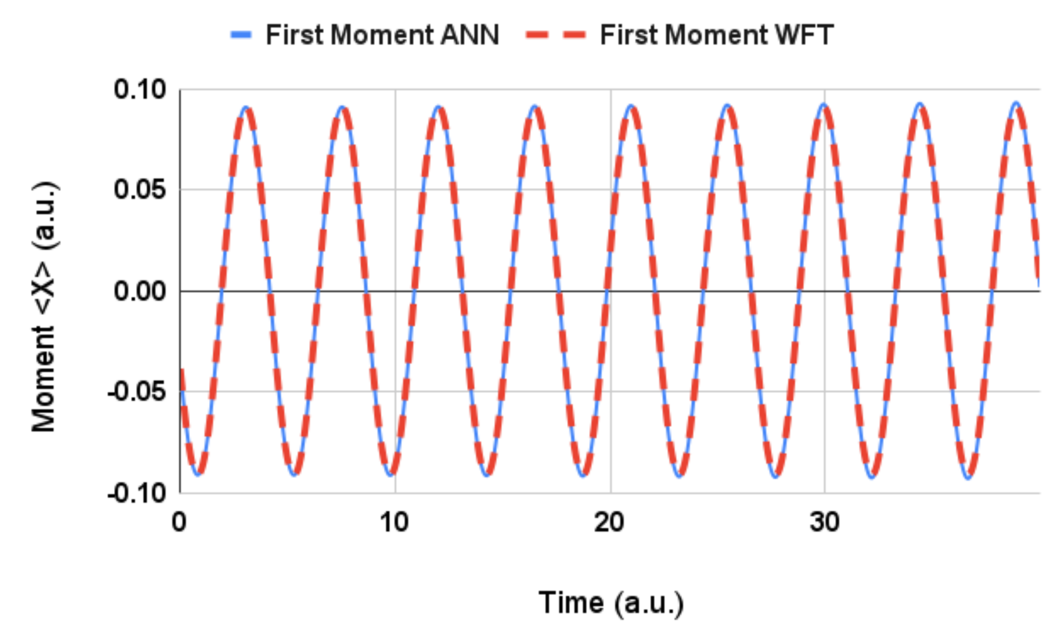




Proof-of-Principle Application to Artificial Neural Network



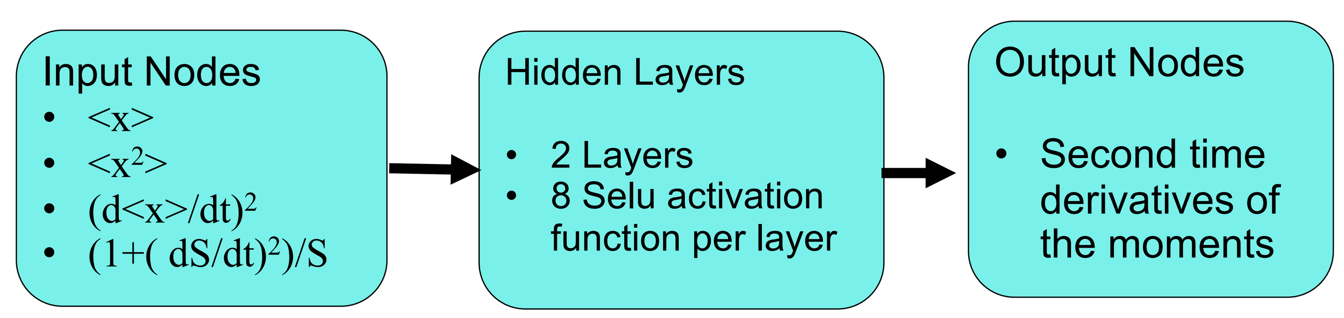


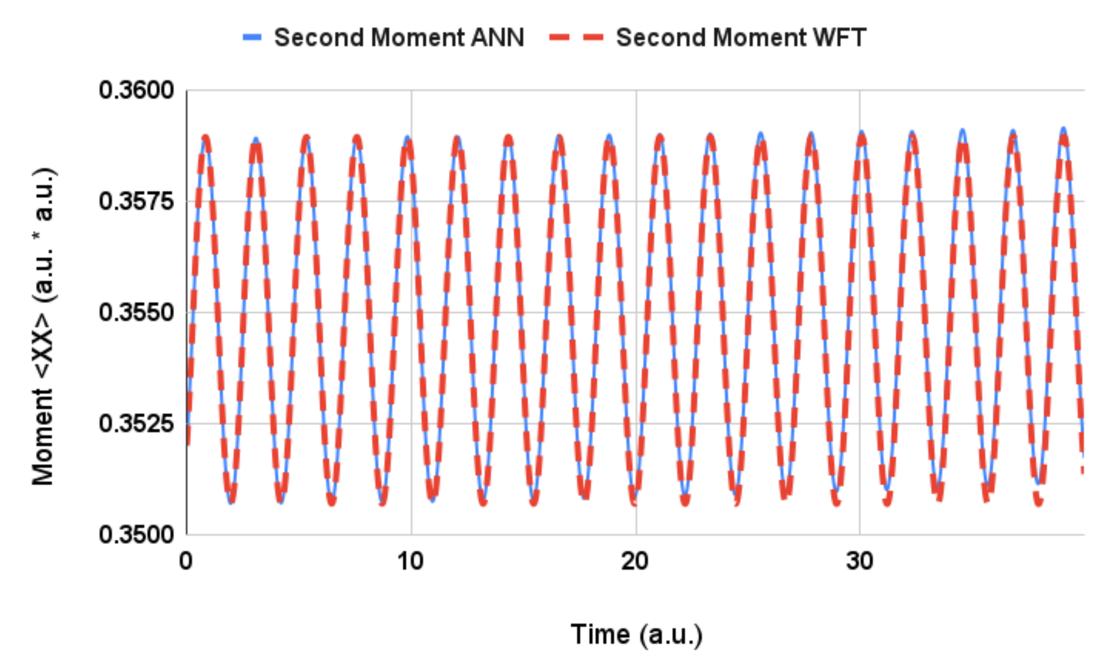


Artificial Neural Network

The artificial neural network (ANN) was trained on data generated through propagating TDSE (wave function theory).

Input descriptors for the ANN were motivated by the analytical solution for the harmonic potential problem.





Acknowledgment: This work was supported by the Chapel Family Fellowship and by the National Science Foundation, under No. OAC-2209858 and No. CHE-1954894.