MESHLESS BASIS SET FOR SOLVING ONE-DIMENSIONAL TIME INDEPENDENT SCHRÖDINGER EQUATION

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This thesis is dedicated to:

My beloved family especially to my parent

and all my friends

They have always been at my side in any endeavor – constantly supportive and seldom critical. I owe them more than they will ever know. I love you all.

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ABSTRACT

The ability of Schrödinger equation in representing the energies and wave function of the molecular system has attracted many scientists to find the best solution for it. Due to the restriction of this equation that can only be solved analytically for the simple molecular models; numerous of numerical methods were introduced to solve it. The Fourier grid Hamiltonian (FGH) method introduced by Marston and Balint-Kurti in 1989 solved the one-dimensional time independent Schrödinger equation for H_2 molecule by using the plane wave basis set and coupling with the Fast Fourier Transform (FFT) technique to reduce the computational time. In this study, we implement the Meshless Element Free Galerkin (MEFG) method to solve the same problem. The localized basis sets adopted in this method and the compactness properties of the weight function lead us to generate a sparse Hamiltonian matrix in finding the eigenvalues and eigenfunctions. The aim of this study is to develop a new numerical approach to solve the one-dimensional time independent Schrödinger equation and as a preliminary research work for us to investigating into the computational quantum mechanics studies.

ABSTRAK

Keupayaan persamaan Schrödinger untuk mencari tenaga elektron dan persamaan gelombang system molekul telah menarik perhatian pakar-pakar sains untuk mencari penyelesaian yang optima untuk persamaan ini. Oleh kerana persamaan ini hanya boleh diselesaikan secara analitik untuk model molekul yang sederhana, justeru itu banyak jenis kaedah berangka telah diperkenalkan. Kaedah *Fourier grid Hamiltonian* (FGH) yang diperkenalkan oleh Marston dan Balint-Kurti pada tahun 1989 berjaya menyelesaikan persamaan satu dimensi Schrödinger yang tak bersandar kepada masa untuk molekul Hidrogen dengan menggunakan set asas gelombang satah dan menggandingkan teknik *Fast Fourier Transform* (FFT) untuk mengurangkan masa pengiraan. Dalam kajian ini, kita telah menggunakan kaedah *Meshless Element Free Galerkin* (MEFG) untuk menyelesaikan masalah yang sama. Set asas setempat yang digunakan dalam kaedah ini serta sifat-sifat kepadatan fungsi pemberat membolehkan kita menjanakan matriks Hamilton yang jarang untuk mencari nilai-nilai dan fungsi-fungsi eigen. Tujuan kajian ini adalah untuk memperkenalkan satu kaedah berangka baru dalam menyelesaikan persamaan Schrödinger tersebut dan sebagai satu permulaan dalam kajian pengiraan mekanik kuantum.

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LIST OF SYMBOLS

h	-	Plank constant
$\hbar$	-	Planck constant divide by 2π
m	-	Mass of atom/molecule
$\Psi(\mathbf{r}, t)$	-	Wavefunction dependent on time
$\mathbf{r}$	-	Vector space in $\mathbf{i}, \mathbf{j}$ and $\mathbf{k}$ direction
t	-	Time
V	-	Potential field or potential energy
ψ	-	Wavefunction or eigenfunction
$T(t)$	-	Function involve of time t
i, j, l	-	Integer index
E	-	Energy of the particle or eigenenergy/eigenvalue
$\hat{\mathcal{H}}$	-	Hamiltonian operator
i	-	Complex number
$y, p_j(x), a_j(\bar{x})$	-	Arbitrary function of x
x	-	Real space coordinate
A_1, A_2, k_a, N, c_1	-	Arbitrary constants
f	-	frequency
c	-	Speed of wave
λ_e	-	Wave length
Δx	-	Spacing between two grid/nodal points
x_i	-	Real space coordinate at node i
A	-	Arbitrary observable
$\hat{A}$	-	Arbitrary operator
n	-	Total number of grid/nodal points
L	-	Length of domain

$\hat{x}$	-	Coordinate operator
k	-	Reciprocal space coordinate
$\hat{T}$	-	Kinetic energy operator
λ_{max}	-	Maximum wave length
$\hat{I}_x$	-	Identity operator
δ_{ij}	-	Knonecker delta function
f_l	-	Discrete Fourier Transform
$\delta(x - x')$	-	Dirac Delta function
$\hat{H}_{ij}$	-	Hamiltonian operator in discrete form
H_{ij}^0	-	Renormalized Hamiltonian matrix
w	-	Circular frequency
k_{wave}	-	Wave number
A_{normal}	-	Normalizing constant
$u(x)$	-	Approximated wave function
$u^h(x)$	-	MLS approximants
Ω	-	Domain
$\mathbf{P}(x)$	-	Complete polynomial of order
q	-	Number of terms in the basis
$\mathbf{a}(x)$	-	Unknown coordinate-dependent coefficients
u_i	-	Nodal parameters
J	-	Weighted discrete L_2 norm
$w(x - x_i)$	-	Weight function
$\mathbf{A}(x), \mathbf{B}(x), \mathbf{K}, \mathbf{V}, \dot{\mathbf{V}}(x),$ $\mathbf{M}, \mathbf{H}, \mathbf{S}, \mathbf{T}, \mathbf{x}, \mathbf{R}, \mathbf{C}, \mathbf{y}, \mathbf{Y}$	-	Arbitrary matrix and vectors
$\mathbf{u}$	-	Vector of a set of u_I
$\mathbf{\Phi}(x)$	-	Vector of a set of shape functions
$\Phi_i(x)$	-	Shape functions
d_i	-	Distance between a nodal point at its neighborhood
d_{mi}	-	Domain of influence size of the Ith node
d_{max}	-	Scaling parameter
c_i	-	Maximum distance to the nearest neighbor

r	-	Normalized radius
$\mathbf{L}$	-	Lower triangular matrix
$\mathbf{I}$	-	Identity matrix
λ	-	Eigenvalue
R_{min}	-	Lower bound of a domain
R_{max}	-	Upper bound of a domain
D_e	-	Well depth
β, γ	-	Constant
x_e	-	Equilibrium internuclear distance (bond length)
ν_e	-	vibrational constant
μ	-	Reduced mass
m_1	-	Mass for first atom
m_2	-	Mass for second atom
$\mathbf{H_1}, \mathbf{M_1}, \mathbf{K_1}, \mathbf{V_1}, \mathbf{u_1}$	-	Reduced matrices and vector
υ	-	Quantum number

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CHAPTER 1

INTRODUCTION

1.1   An Introduction to Quantum Mechanics

Quantum mechanics is one of the most common models that are used in molecular modeling. The chemical reaction is due to the motion of electrons within reacting molecules where the bonds are broken and formed. Quantum mechanical methods able to represent the electrons in calculation and enables us to derive its properties which depend on the electronic distribution. This is important for ones to mimic the behavior of molecules and molecular systems.

In early stage, quantum mechanical methods were restricted to atomic, diatomic or highly symmetrical systems which could be solved by hand. However, with the rapid development and research blooming all these years to invariably associate this technique with the computer technology, we are now able to perform calculations on real molecular systems that required a lot of complicated calculations, Leach (2001).

1.2   Schrödinger Equation as a Gateway to Quantum Mechanical Studies

Understanding and handling of Schrödinger equation is essential for ones to access quantum mechanics studies. The full, time-dependent form of this equation is

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V\right\}\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} \tag{1.1}$$

This equation represents a single particle of mass m moving through a space (given by $\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ in 3D) and time t under the influence of an external field V (which is often refer to potential). The universal constant, $\hbar$ is given as follow where h is the Planck's constant.

$$\hbar = \frac{h}{2\pi} \tag{1.2}$$

and $$i = \sqrt{-1}$$

The wave function $\Psi(\mathbf{r},t)$ of position and time is also known as state function which describes the physical condition or motion of a particle. When the external potential V is independent of time then we can construct a solution to the time dependent Schrödinger equation of the form $\Psi(\mathbf{r},t) = \psi(\mathbf{r})T(t)$, which is the technique of separation of variables.

It is more common for us to consider that the potential V is independent of time, which enables us to derive the time-independent Schrödinger equation.

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right\}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{1.3}$$

Here, E is the energy of the particle and $\nabla^2 = \partial^2/\partial x^2$ in one dimensional. The left-hand side of Equation (1.3) is usually written as $\hat{\mathcal{H}}\psi$, where $\hat{\mathcal{H}}$ is the Hamiltonian operator:

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \tag{1.4}$$

This reduces the one-dimensional Schrödinger equation to

$$\hat{\mathcal{H}}\psi(x, t = 0) = E\psi(x, t = 0) \tag{1.5}$$

and it is known as the partial differential eigenvalue equations where the Hamiltonian operator acts on the eigenfunction and returns the function multiplied by a scalar (the eigenvalue). In this equation, $\psi(x, t = 0)$ is the eigenfunction and E the eigenvalue and it is necessary for us to find the values of them in order to solve the Schrödinger equation. The Schrödinger equation is a second-order differential

equation as it involves the second derivative of $\psi(x, t = 0)$ and a simple example is shown below.

$$\frac{d^2y}{dx^2} = ry \qquad (1.6)$$

The solution of Equation (1.6) is in the form of $y = A_1 \cos k_a x + A_2 \sin k_a x$, where A_1, A_2 and k_a are constants.

1.3   Problem Background

In quantum mechanics, it is impossible for us to perform measurements on the atomic and subatomic systems without perturbs it. The act of measurement induces non negligible disturbances on the system. For example, consider an experiment that measures the position of a hydrogenic electron. The electron need to be bombarded with an electromagnetic radiation (photons) of energies higher than

$$hf = h\frac{c}{\lambda_e} = h\frac{3 \times 10^8}{10^{-10}} \sim 10^4 \text{ eV} ;$$

$$h = \text{Planck constant}, f = \text{frequency}, c = \text{speed of light}, \lambda_e = \text{wave length}$$

When such photons strike the electron, not only the system will be perturbed but also the electrons can be completely knocked off from its orbit; recall that the ionization energy of the hydrogen atom is just 13.5eV. Thus, the mere act of measuring the position of the electron disturbs it substantially.

In theory, we can represent the position of electrons by a wavefunction and denotes the measuring device by an operator. The abstract kets $|\psi\rangle$, like wavefunctions, are elements of Hilbert space and therefore they are often used to represent the system completely in quantum mechanics. Before measuring an observable A, a system in the state $|\psi\rangle$ can be represented by a linear superposition of eigenstates $|\psi_i\rangle, i = 1, 2, \ldots, n$ of the corresponding operator $\hat{A}$. After carrying out the measurement, the system will be in one of the eigenstates of the operator, and the result obtained is the eigenvalue a_i, Zettili (2009):

$$|\psi\rangle = \sum_i |\psi_i\rangle \langle\psi_i|\psi\rangle = \sum_i a_i |\psi_i\rangle \qquad (1.7)$$

However, only a few of Schrödinger equations have simple solutions and can be solved exactly. These cases are classified as "exactly solvable" problems. A mixture of well-tested analytic and numerical methods is then selected to solve the Schrödinger equation based on the desired degree of accuracy. Nevertheless, some significance errors might be truncated in the process of simplification or in the chosen numerical method. Hence, we are left to our own devices opting for a numerically and physically acceptable solution.

Expansion of the wavefunctions in basis sets has been well recognized throughout many years. Basis set is couple of linear combinations of simpler, linearly independent, and mutually orthogonal functions that allow us to generate any other function belonging to that wavefunction spaces. Theoretically, such sets must be infinite in size; in practice these are truncated due to the limitations in computational.

This irreconcilable conflict has brought up the curiosity in inventing the "best" basis sets. Although these basis sets are distinctive among each other, however they are fulfilling the completeness requirements and emphasizing salient features of the wavefunctions to be computed. Some successful examples of basis sets are the Gaussian home base functions in solid helium, harmonic oscillator functions for nuclei, Slater functions in atoms and molecules. However, considerable criticism can be leveled against the mathematical behavior of most basis functions, Leach (2001).

In year 1989, Fourier Grid Hamiltonian (FGH) method which implemented Fast Fourier transform (FFT) technique was introduced by C.C. Marston and G.G. Balint-Kurti to solve the bound state eigenvalues and eigenfunctions of the Schrödinger equation numerically. In order to coupling the Fast Fourier Transform tool, the common basis set to be used was plane wave basis set. However, it is well

known that plane wave basis set has convergence problem and required special techniques such as FFT to achieve faster convergence.

1.4   Statement of the Problem

In this research, we are using the Meshless Element Free Galerkin (MEFG) method which associates with the localized basis set as an alternative approach to calculate the bound state eigenvalues and eigenfunctions of the Schrödinger equation. This localized basis set is in the form of polynomial functions and represents the wavefunctions in real space. Therefore, we do not require the complex transformation between real space (coordinate representation) and reciprocal space (momentum representation) by using the Fourier transform technique.

The Schrödinger equation mentioned above can be written in many forms. In this research work, the one-dimensional time independent Schrödinger equation defines on a domain $R_{min} \leq x \leq R_{max}$ that we are solving has the final form of

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \right)\psi(x) = E\psi(x)$$

and subjects to the boundary conditions

$$\psi(R_{min}) = 0$$
$$\psi(R_{max}) = 0$$

1.5   Simulation Using C Programming Language

A program to solve the eigenvalues and eigenfunctions of the Schrödinger equation numerically by the MEFG method was developed by using the C Programming language.

1.6   Objectives of Study

The objective of the study is to understand the current quantum mechanical methods that can be used to solve the one dimensional Schrödinger equation for atoms with more than one electron or molecules such as:

(i)   To solve bound state eigenvalue problem of a Morse potential for H_2 using FGH method.

(ii)   To solve the same problem using the MEFG method which using localized basis set.

1.7   Scope of Study

This research will focus on solving the one dimensional eigen system in the Schrödinger equations for H_2 molecule. The Fourier grid Hamiltonian (FGH) method that uses plane wave basis set and Fast Fourier Transform (FFT) as a tool to speed up the calculation is studied and the same problem is then solved by using the Meshless Element Free Galerkin (MEFG) method that associates with the localized basis set and produce a sparse matrix in the final eigen system.

In order to justify whether the selection for using MEFG method is appropriate, the final result can be compared with the results obtained by the FGH method and also the analytical approach.

1.8   Significance of Study

This study is a preliminary research work for us to investigating into the computational quantum mechanics studies. The model using localized basis set aims to simplify the eigensystem which might save significant steps in calculation or produce a set of better results.

1.9   Thesis Organization

This report consists of five chapters. Chapter 1 contains the introduction of the quantum mechanics, brief introduction to the Schrödinger equation as a gateway to understand the quantum mechanical studies, problem statement, program development, objectives, scope of study, significance of study and also the thesis organization.

Chapter 2 reviews the background of Schrödinger equation and some numerical methods used by some researchers in solving this problem. In particular, the Fourier grid Hamiltonian method which couplings with the Fast Fourier transform technique is discussed in details.

Chapter 3 explains the difference between plane wave and localized basis set methods. The Meshless Element Free Galerkin method is introduced as an alternative approach to solve the one-dimensional time independent Schrödinger equation.

Chapter 4 presents a case study in solving one-dimensional time independent Schrödinger equation for the H_2 molecule. Our results are compared with the one obtained from FGH method and also the analytical results. Some discussion on the comparison of the results will also be discussed in this chapter.

Lastly, Chapter 5 gives the conclusion of the case study and overall conclusion for this thesis. Recommendation is also given to improve this method.

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