Smoothed Particle Method for Real-Space Electronic Structure Calculations

Soichiro Sugimoto and Yasunari Zempo
Computer and Information Sciences, Hosei University,
3-7-2 Kajino, Koganei, Tokyo 184-8584, Japan
E-mail: 12t0007@cis.k.hosei.ac.jp

Abstract. We present a meshfree particle method for real-space electronic structure calculations based on symmetric smoothed particle hydrodynamics (SSPH). As a simple example, we applied SSPH to the Schrödinger equation for a one-dimensional harmonic oscillator. The results calculated using SSPH are in good agreement with analytical solutions. We compared results for different cases of kernel function, smoothing length, number of particles, and the order of the Taylor series expansion. The results using SSPH and the higher-order finite-difference method are also compared. Our results indicate that SSPH can be applied to real-space electronic structure calculations that require high accuracy.

1. Introduction
The real-space approach is widely used for electronic structure calculations based on density functional theory [1, 2, 3]. In particular, it is used for large systems that include many atoms, because a real-space mesh is suitable for large-scale parallel computing. The real-space approach also allows the capture of a clear physical image because it does not use an explicit basis such as a plane wave or Gaussian basis sets. For the simplest real-space implementation, the higher-order finite-difference method is employed as the discretization technique [1, 2]. A regular mesh is efficient because it produces a sparse and structured matrix. However, a regular mesh has equal spacing everywhere, which seems to be an inefficient distribution of computation points. There are also real-space implementations using finite-element and meshfree methods [1, 4, 5]. These methods have an advantage in their non-uniform distribution of computation points, which also reduces computational costs.

Smoothed particle hydrodynamics (SPH) [6, 7, 8, 9] is a typical meshfree particle method, in which the system is represented by a finite set of arbitrarily distributed particles without using any mesh. SPH is widely used to solve hydrodynamic equations in various areas such as astrophysics and magnetohydrodynamics [10]. In addition, the SPH-based method is applied to non-hydrodynamic partial differential equations such as the wave equation, diffusion equation, Poisson’s equation, and Maxwell’s equations [11, 12, 13, 14]. However, there are few studies addressing the use of SPH for electronic structure calculations.

The SPH-based method provides an efficient real-space technique because the computation points can be arbitrarily distributed. Since SPH is known for its low accuracy [12], the corrective smoothed particle method (CSPM) [15], the modified smoothed particle hydrodynamics (MSPH)
[16], and the symmetric smoothed particle hydrodynamics (SSPH) [17, 18] have all been proposed as alternatives. These methods improve the accuracy of SPH using the Taylor series expansion.

In this study, we employ the SSPH method because it is the simplest method in the higher-order series expansion. This study evaluates the accuracy of SSPH for electronic structure calculation applications. For simplicity, we applied SSPH to the Schrödinger equation for a one-dimensional harmonic oscillator, whose analytical solution is well known. In the evaluation, we focused on the relative error of the eigenvalue. The result is then compared to the higher-order finite-difference method.

The paper is organized as follows. The formulation of the SSPH method is presented in the next section. The numerical tests are shown in section 3. Finally, we summarize and discuss our conclusions in the last section.

2. Methods
First, we briefly introduce the SSPH method and then address the discretization of the Schrödinger equation.

2.1. Symmetric Smoothed Particle Hydrodynamics (SSPH)
In SPH, the field function is approximated using integral representation, and the system is represented by a finite number of particles. The concept of the integral representation of a field function $\psi(x)$ starts from the following identity.

$$\psi(x') = \int_{\Omega} \psi(x) \delta(x - x') dx.$$  \hspace{1cm} (1)

If the Dirac delta function is replaced by the function $W(x - x', h)$, which is called the kernel function, the integral representation is approximated as follows:

$$\psi(x') \approx \int_{\Omega} \psi(x) W(x - x', h) dx,$$  \hspace{1cm} (2)

where $h$ is the smoothing length. A Gaussian function is a typical kernel function since the kernel function approximates the delta function.

$$W(x - x', h) = W(|x - x'|, h) = W(r, h) = \frac{1}{h\sqrt{\pi}} \exp \left( -\frac{r^2}{h^2} \right).$$  \hspace{1cm} (3)

Figure 1. Wendland and Gaussian kernel functions in one-dimensional space, where $h$ is the smoothing length. The Wendland kernel is truncated at $2h$, whereas the Gaussian has a long tail.
In this study, we employ the Wendland kernel \[19, 20\].

\[
W(r, h) = \begin{cases} 
\frac{3}{4h} \left(1 - \frac{r}{2h}\right)^5 \left(2 \left(\frac{r}{h}\right)^2 + \frac{5}{2} \frac{r}{h} + 1\right) & (0 \leq \frac{r}{h} \leq 2) \\
0 & \left(\frac{r}{h} \geq 2\right)
\end{cases}
\]  

(4)

SSPH corrects the approximation of SPH using the Taylor series expansion. Using the Taylor series expansion of \(\psi(x)\), the right-hand side of Eq. (2) and its moments can be written as follows:

\[
\int_{\Omega} \psi(x)Wdx = \psi(x_i)\int_{\Omega} Wdx + \frac{\partial \psi}{\partial x_i} \int_{\Omega} (x - x_i)Wdx + \frac{1}{2} \left(\frac{\partial^2 \psi}{\partial x_i^2}\right) \int_{\Omega} (x - x_i)^2Wdx + \cdots,
\]

\[
\int_{\Omega} (x - x_i)\psi(x)Wdx = \psi(x_i)\int_{\Omega} (x - x_i)Wdx + \left(\frac{\partial \psi}{\partial x_i}\right) \int_{\Omega} (x - x_i)^2Wdx + \frac{1}{2} \left(\frac{\partial^2 \psi}{\partial x_i^2}\right) \int_{\Omega} (x - x_i)^3Wdx + \cdots,
\]

\[
\int_{\Omega} (x - x_i)^m\psi(x)Wdx = \psi(x_i)\int_{\Omega} (x - x_i)^mWdx + \left(\frac{\partial \psi}{\partial x_i}\right) \int_{\Omega} (x - x_i)^{m+1}Wdx + \frac{1}{2} \left(\frac{\partial^2 \psi}{\partial x_i^2}\right) \int_{\Omega} (x - x_i)^{m+2}Wdx + \cdots.
\]

(5)

Solving the following linear equation, \(\psi(x_i)\) and its derivatives can be obtained.

\[
\begin{bmatrix}
K_{11} & K_{12} & \cdots & K_{1(m+1)} \\
K_{21} & K_{22} & \cdots & K_{2(m+1)} \\
\vdots & \vdots & \ddots & \vdots \\
K_{(m+1)1} & K_{(m+1)2} & \cdots & K_{(m+1)(m+1)}
\end{bmatrix}
\begin{bmatrix}
\psi_1 \\
\frac{\partial \psi}{\partial x_i}|_{x_i} \\
\frac{1}{2} \left(\frac{\partial^2 \psi}{\partial x_i^2}\right)|_{x_i} \\
\vdots \\
\frac{1}{m!} \left(\frac{\partial^m \psi}{\partial x_i^m}\right)|_{x_i}
\end{bmatrix}
= \begin{bmatrix}
\int_{\Omega} \psi(x)W(x - x_i, h)dx \\
\int_{\Omega} (x - x_i)\psi(x)W(x - x_i, h)dx \\
\int_{\Omega} (x - x_i)^2\psi(x)W(x - x_i, h)dx \\
\vdots \\
\int_{\Omega} (x - x_i)^m\psi(x)W(x - x_i, h)dx
\end{bmatrix},
\]

(6)

where

\[
K_{IJ} = \int_{\Omega} (x - x_i)^{I-1}(x - x_i)^{J-1} W(x - x_i, h)dx \quad (I, J = 1, 2, \cdots, m + 1).
\]

(7)

In the SPH-based method, the system is represented by a finite number of particles. Therefore, the integral representation can be converted to a discretized form of summation over all particles. If the small region \(dx\) at the location of the particle \(j\) is replaced by the finite volume \(\Delta V_j\),

\[
\int_{\Omega} (x - x_i)^k \psi(x)W(x - x_i, h)dx \approx \sum_{j=1}^{N} (x_j - x_i)^k \psi(x_j)W(x_j - x_i, h)\Delta V_j
\]

\[
= \sum_{j=1}^{N} (x_j - x_i)^k \psi(x_j)W_{ij}\Delta V_j \quad (k = 0, 1, 2, \cdots, m).
\]

(8)

The particle number density is defined as

\[
n(x) \equiv \sum_{a=1}^{N} \delta(x_a - x).
\]

(9)
It can be approximately expressed as

\[ n(x_i) \approx \sum_{j=1}^{N} W(x_j - x_i, h). \]  

The finite volume of the particle \( i \) is equivalent to

\[ \Delta V_i = \frac{1}{n(x_i)} = \frac{1}{n_i}. \]  

Finally, the integral representation can be discretized as

\[
\int_{\Omega} (x - x_i)^k \psi(x) W(x - x_i, h) dx \approx \sum_{j=1}^{N} (x_j - x_i)^k \psi(x_j) W_{ij} \frac{1}{n_j} \quad (k = 0, 1, 2, \cdots, m). \tag{12}
\]

Thus, Eq.(6) is transformed to the discretized form.

2.2. Discretization of the Schrödinger equation using SSPH

The one-dimensional Schrödinger equation is

\[
\left[ -\frac{1}{2} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = \varepsilon \psi(x). \tag{13}
\]

Considering Eqs. (6) and (12), we can easily obtain the discretized form of the wave function \( \psi(x) \) and its second derivative. The Schrödinger equation at the location of the particle \( i \)

\[
-\frac{1}{2} \frac{\partial^2 \psi}{\partial x^2} \bigg|_{x_i} + V(x) \psi(x_i) = \varepsilon \psi(x_i) \tag{14}
\]

can be expressed using SSPH:

\[
\begin{bmatrix}
V(x_i) & 0 & \sum_{j=1}^{N} \psi(x_j) W_{ij} \Delta V_j \\
0 & -1 & \sum_{j=1}^{N} (x_j - x_i) \psi(x_j) W_{ij} \Delta V_j \\
-1 & 0 & \sum_{j=1}^{N} (x_j - x_i)^2 \psi(x_j) W_{ij} \Delta V_j \\
\vdots & \vdots & \vdots \\
0 & \sum_{j=1}^{N} (x_j - x_i)^m \psi(x_j) W_{ij} \Delta V_j
\end{bmatrix}
K^{-1}
\begin{bmatrix}
N \\
0 \\
\vdots \\
0
\end{bmatrix}
= \varepsilon
\begin{bmatrix}
N \\
0 \\
\vdots \\
0
\end{bmatrix}
K^{-1}
\begin{bmatrix}
N \\
0 \\
\vdots \\
0
\end{bmatrix}
\begin{bmatrix}
\sum_{j=1}^{N} (x_j - x_i)^2 \psi(x_j) W_{ij} \Delta V_j \\
\sum_{j=1}^{N} (x_j - x_i)^m \psi(x_j) W_{ij} \Delta V_j
\end{bmatrix}. \tag{15}
\]

The matrix equation of the generalized eigenvalue problem can be obtained as

\[
Hu = \varepsilon Su, \tag{16}
\]
where

\[
H_{ij} = \begin{bmatrix}
V(x_i) & 0 & -1 & 0 & \cdots & 0 \\
0 & (x_j - x_i)W_{ij}\Delta V_j & (x_j - x_i)^2W_{ij}\Delta V_j & \cdots & \cdots & (x_j - x_i)^mW_{ij}\Delta V_j \\
\vdots & \vdots & \vdots & \ddots & \ddots & \vdots \\
0 & 0 & 0 & \cdots & (x_j - x_i)^mW_{ij}\Delta V_j & (x_j - x_i)^{m+1}W_{ij}\Delta V_j
\end{bmatrix}
K^{-1}
\begin{bmatrix}
W_{ij}\Delta V_j \\
(x_j - x_i)W_{ij}\Delta V_j \\
(x_j - x_i)^2W_{ij}\Delta V_j \\
\vdots \\
(x_j - x_i)^mW_{ij}\Delta V_j
\end{bmatrix}
, \quad S_{ij} = \begin{bmatrix}
1 & 0 & 0 & \cdots & 0 \\
0 & 1 & 0 & \cdots & 0 \\
0 & 0 & 1 & \ddots & \vdots \\
\vdots & \vdots & \ddots & \ddots & 0 \\
0 & 0 & \cdots & 0 & 1
\end{bmatrix}
K^{-1}
\begin{bmatrix}
W_{ij}\Delta V_j \\
(x_j - x_i)W_{ij}\Delta V_j \\
(x_j - x_i)^2W_{ij}\Delta V_j \\
\vdots \\
(x_j - x_i)^mW_{ij}\Delta V_j
\end{bmatrix}
\]  \tag{17}

and \( u = [\psi(x_1), \psi(x_2), \cdots, \psi(x_N)]^T \).

3. Numerical Tests

In this section, we discuss the accuracy of the eigenvalue. We first solve the Schrödinger equation for a one-dimensional harmonic oscillator

\[
\left[-\frac{1}{2} \frac{\partial^2}{\partial x^2} + V(x)\right] \psi(x) = \varepsilon \psi(x), \quad V(x) = \frac{1}{2} \omega^2 x^2. \tag{18}
\]

For simplicity, we use \( \omega = 1 \). The particles are uniformly distributed with constant spacing \( \Delta x \) on the region \([-20, 20]\). The number of particles is \((40/\Delta x + 1)\).

Figure 2 shows the relative errors of the lowest eigenvalue, which is calculated using SSPH based on the \( m \)-th order Taylor series expansion. In this figure, \( E_{\text{SSPH}} \) is the eigenvalue of the SSPH method, and \( E \) is the analytical solution. The results in Fig.2(a) are for the cases of \( m = 2, 5, 8, 11, \) and 14. The smoothing length \( h \) is changed with the order \( m \), \( h = 1.5\Delta x, 3.2\Delta x, 4.5\Delta x, 6.0\Delta x, \) and 7.5\( \Delta x \), respectively. The accuracy becomes higher as the order of the Taylor series expansion increases. Using the higher-order Taylor series

\[\text{Figure 2.} \quad \text{Convergence of the lowest eigenvalue for one-dimensional harmonic oscillator. (a) Results using SSPH based on the } m \text{-th order Taylor series expansion. (} m = 2, 5, 8, 11, \text{ and 14.)} \quad \text{(b) Results using SSPH based on the 14-th order Taylor series expansion. The smoothing length is } h = 5.0\Delta x, 6.0\Delta x, \text{ and } 7.0\Delta x.\]
expansion with SSPH, we can obtain sufficient accuracy for electronic structure calculations. The computational cost to solve Eq.(17) increases with the order of the series expansion. As such order selection should be made according to the required accuracy.

A comparison of results using different smoothing lengths is shown in Fig.2(b). The Taylor series is expanded up to the 14-th order term, and the smoothing length is $h = 5.0\Delta x$, $6.0\Delta x$, and $7.0\Delta x$. A shorter smoothing length gives higher accuracy at the same particle spacing $\Delta x$, since it gives a kernel function closer in shape to the delta function. The results indicate that a shorter smoothing length should be employed. However, a smoothing length that is too short makes the SSPH inconsistent and prevents us from solving the eigenvalue problem in Eq.(16). A smoothing length too long also gives incorrect results. We believe that the loss of locality causes these poor results. An appropriately short smoothing length should be employed to give correct results. The optimal selection of the smoothing length may be a goal in our future research.

Figure 3 shows a comparison of the SSPH results using Wendland and Gaussian kernels. The Taylor series of the SSPH is expanded up to the second-order term. The smoothing length is $h = 1.0\Delta x$. The results show that the Wendland kernel yields higher accuracy than the Gaussian kernel. The Wendland function gives almost the same accuracy as the three-point finite-difference method. As compared with the Gaussian kernel, the Wendland kernel is more

![Figure 3.](image1)

**Figure 3.** Convergence of the lowest eigenvalue for a one-dimensional harmonic oscillator. These are the results using SSPH and the three-point finite-difference method (triangle). The Taylor series of SSPH is expanded up to the second-order term. The Gaussian function (square) and the Wendland function (circle) are employed as the kernel functions.

![Figure 4.](image2)

**Figure 4.** Convergence of the lowest eigenvalue for a one-dimensional harmonic oscillator. These are the results using SSPH (circle) and the higher-order finite-difference method, with three, five, seven, and nine point finite differences.
similar to the delta function. We consider this to be the reason that Wendland kernel gives higher accuracy.

In Fig.4, results using the higher-order finite-difference method and SSPH are compared because the higher-order finite-difference method is frequently employed for real-space electronic structure calculations. To achieve the same accuracy using SSPH, we need an SSPH Taylor series up to the 14-th order term and a smoothing length of $h = 5.0\Delta x$. The SSPH results give higher accuracy than the nine-point finite-difference method when $\Delta x = 0.3, 0.2,$ and 0.1.

4. Conclusions and Discussion
We presented a method for real-space electronic structure calculations based on a meshfree particle method. The SSPH method has been applied to solve the Schrödinger equation of a one-dimensional harmonic oscillator. We investigated the effect of kernel function, smoothing length, and the order of the Taylor series expansion. The SSPH method based on the higher-order Taylor series expansion provides similar accuracy as the higher-order finite-difference method. SSPH may be applied in real-space electronic structure calculations that require high accuracy.

With the same particle spacing $\Delta x$, a shorter smoothing length gives higher accuracy, since it gives a kernel function closer in shape to the delta function. Our results indicate that we should employ an appropriately short smoothing length. The number of particles required in the support domain is determined so as to avoid any singularity of the SSPH system. We believe that a better smoothing length is determined from the number of particles and a nearest neighbor search algorithm. For our future study, we plan to study non-uniform particle distribution and methods for selecting an optimal smoothing length.

Acknowledgments
The authors would like to acknowledge Professor S. S. Kano for his useful discussions and encouragement. This study was partially supported by a JSPS Grants-in-Aid for Scientific Research (C) Grant number 25390158, Sumitomo Chemical Co. Ltd. and Simulatio Corporation.

References
[1] Beck T L 2000 Rev. Mod. Phys. 72 1041-80
[2] Chelikowski J, Troullier N, Wu K, and Saad Y 1994 Phys. Rev. B 50 11355
[3] Zempo Y, Akino N, Ishida M, Ishitobi M, and Kurita Y 2008 J. Phys. Cond. Matt. 20 064231
[4] Tsuchida E and Tsukada M 1995 Phys. Rev. B 52 5573-78
[5] Jun S 2004 Int. J. Numer. Meth. Engrg. 59 1909-23
[6] Gingold R A and Monaghan J J 1977 Mon. Not. Roy. Astr. Soc. 181 375-89
[7] Lucy L B 1977 Astron. J. 82 1013-24
[8] Monaghan J J 1988 Comput. Phys. Commun. 48 89-96
[9] Liu G R and Liu M B 2003 Smoothed Particle Hydrodynamics: a meshfree particle method (Singapole: World Scientific)
[10] Price D J 2012 J. Comput. Phys. 231 759-94
[11] Laguna P 1995 Astrophys. J. 439 814-21
[12] Stranex T and Wheaton S 2011 Comput. Methods Appl. Mech. Engrg. 200 392-402
[13] Toscano E, Blasi G D and Tortorici A 2012 Appl. Math. Comput. 218 8906-16
[14] Ala G, Francomano E, Tortorici A, Toscano E and Viola F 2006 J. Comput. Appl. Math. 191 194-205
[15] Chen J K, Beraun J E, and Jih C J 1999 Comput. Mech. 24 273-85
[16] Zhang G M and Batra R C 2004 Comput. Mech. 34 137-46
[17] Batra R C and Zhang G M 2008 Comput. Mech. 41 527-45
[18] Zhang G M and Batra R C 2009 Comput. Mech. 43 321-40
[19] Wendland H 1995 Adv. Comput. Math. 4 389-96
[20] Monaghan J J and Kajtar J B 2009 Comput. Phys. Commun. 180 1811-20