Development of the SSPH Method for Real-Space Electronic Structure Calculations

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Abstract. We have applied symmetric smoothed particle hydrodynamics (SSPH) to real-space electronic structure calculations. The electronic structure of a simple atom such as hydrogen, helium and lithium is calculated. The results of SSPH are compared to that of the higher-order finite difference method (FD), and are in good agreement with that of FD. Our results indicate that SSPH can be applicable to the electronic structure calculations that require high accuracy.

1. Introduction
The real-space approach is widely used for electronic structure calculation based on density functional theory [1, 2, 3]. In particular, it is used for large systems including many atoms, because a real-space mesh is suitable for large-scale parallel computing. The high-order finite-difference method (FD) is frequently employed in the calculation on a regular mesh. However, it has equal resolution everywhere, which seems to be an inefficient distribution of computation points and to be expensive. If non-uniform distribution of computation points can be used, we can significantly reduce computational costs.

Smoothed Particle Hydrodynamics (SPH) 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 applied to hydrodynamic problems which deal with complex shapes, large deformations and free surfaces. Recently, the SPH based method has been applied to solve non-hydrodynamic partial differential equations such as the wave equation, the diffusion equation, Maxwell’s equations and Poisson’s equation [4, 5, 6, 7]. On the other hand, there are few studies for the electronic structure calculation [8].

The SPH based method may lead to an efficient real-space technique because of arbitrarily distributed computation points. However, it is generally known that standard SPH method has low accuracy [9]. In considering the application to practical electronic structure calculation, obtaining the almost equal accuracy to finite-difference method by using meshfree particle method is one of the problems. As one of the improved techniques, Symmetric Smoothed Particle Hydrodynamics (SSPH) [10, 11] have been proposed. This method successfully increases the accuracy of standard SPH using Taylor series expansion.

In this paper, we have employed SSPH since it is the simplest method in the higher-order series expansion. The purpose of this paper is evaluation of SSPH for the electronic structure calculation. For simplicity, we have applied SSPH to the Kohn-Sham equation [12, 13] to solve a
simple atom such as hydrogen, helium, and lithium. In the evaluation, we focus on the relative
error of the eigenvalue. The result is compared to that of FD.

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

2. Method
In SPH, the wave function is approximated using integral form, and the system is represented by
a finite number of particles. The concept of the integral representation of a wave function
\( \psi(r) \) starts from the following identity. The delta function is replaced by a kernel function
\( W(r, h) \).

\[
\psi(r) = \int_{\Omega} \psi(r') \delta(r - r') \, dr' \simeq \int_{\Omega} \psi(r') W(r - r', h) \, dr',
\]

where \( h \) is the smoothing length. As the kernel function, we adopt the Wendland function [14].

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

SSPH corrects the approximation of SPH using the Taylor series expansion. Using the Taylor
series expansion of \( \psi(r) \), the right-hand side of Eq. (1) and its moments can be rewritten as
follows.

\[
\int_{\Omega} \psi(r') W(r - r', h) \, dr' \simeq \sum_{l=0}^{m} \left( \int_{\Omega} (r - r_i)^{k+l} W(r - r_i, h) dr \right) \left( \frac{1}{l!} \frac{\partial^l \psi}{\partial r^l} \right) \bigg|_{r_i}, \quad (k = 0, 1, \ldots, m)
\]

This expansion can be expressed by the simultaneous linear equation \( P = KD \), where the integral
Eq. (3) is replaced by the summation of the particles. As the small volume of the \( j \) th
particles around the particle \( i \) is expressed \( \Delta V_j \),

\[
P = \begin{pmatrix} P_k \end{pmatrix}, \quad P_k = \sum_{j} (r_j - r_i)^k \psi(r_j) W_{ij} \Delta V_j
\]

\[
K = \begin{pmatrix} K_{kl} \end{pmatrix}, \quad K_{kl} = \left( \int_{\Omega} (r - r_i)^{k+l} W(r - r_i, h) dr \right)
\]

\[
D = \begin{pmatrix} D_l \end{pmatrix}, \quad D_l = \left( \frac{1}{l!} \frac{\partial^l \psi}{\partial r^l} \right) \bigg|_{r_i}
\]

where \( W_{ij} = W(r_j - r_i, h) \).

The electronic structure calculation is performed within the framework of LDA [12, 13].
Taking account of \( D_0 = \psi(r_i) \) and \( D_2 = \frac{1}{2} \frac{\partial^2 \psi(r_i)}{\partial r^2} |_{r_i} \), the Kohn-Sham equation at the position of
the \( i \) th particle in SSPH can be written as

\[
(V(r_i) \quad 0 - 1 \quad \ldots \quad 0) D = (\varepsilon \quad 0 \quad 0 \ldots \quad 0) D,
\]
where \( V(\mathbf{r}) = V_{ec}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \). As an ionic potential \( V_{ec}(\mathbf{r}) \) we use, \( V_H(\mathbf{r}) \) is the Hartree potential, and \( V_{XC}(\mathbf{r}) \) is the exchange-correlation potential. From the electronic charge density \( \rho(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2 \), the Hartree and exchange-correlation potential is determined. In SSPH, the particle position is arbitrarily distributed. However, we have to calculate \( K^{-1} \) in each particle position, and to be careful to keep the matrix \( K \) regular.

3. Results and discussion

In the expression of the SSPH discretization, we solve Eq.(5) for simple atoms such as hydrogen, helium, and lithium. To solve the electronic structure of the atom, there is various conventional computational programs (AT) with high accuracy. Thus, we use it for the evaluation of the calculation of SSPH together with that FD. The SSPH particles are placed on the same regular mesh point, because the results are compared with those of FD. The calculation system was a cube 16 a.u. on a side. The particles of SSPH are regularly distributed on the same spacing points with the distance \( \Delta x = 0.2 \) a.u..

| Table 1. 1s orbital energies. |
|-----------------------------|
|                            | SSPH  | FD    | AT    |
| H                           | -0.230| -0.230| -0.260|
| He                          | -0.543| -0.547| -0.570|
| Li (2s)                     | -0.094| -0.965| -0.128|
| (1s)                        | -1.722| -1.728| -1.922|

Using the 1s orbital energy, the results of SSPH, FD, and AT is listed on Table 1. As for Lithium, the 2s orbital energy was also calculated. The results are graphically shown in Fig.1. The results of SSPH and FD are also compared with those of AT. The results of SSPH are in good agreement with those of FD. However, there are some errors between SSPH and AT. We adopted that the number of particles of SSPH was the same that of FD. Also there is no correction on the boundary of the system. This basically causes the difference between SSPH and AT.

![Figure 1. Comparison of 1s orbital energies. Left hand sides and the other side show the results of SSPH, and those of FD, respectively.](image)

Similar to the procedure as expressed in Eq.(5), we can easily derive the SSPH form of the Poisson equation. We solved the Poisson equation \( \nabla^2 V_H(\mathbf{r}) = -4\pi \rho(\mathbf{r}) \), using SSPH. The calculated charge profiles are shown in Fig.2 and Fig.3. The calculated Hartree energy is in good
agreement in the region far from the core $V_H(r) \simeq Z_n/r$. In the vicinity of the core, the number of the particles is too few to describe the steep change of $V_H(r)$. Figure 3 shows the calculated Hartree energy profile of He as a function of distance from the core. In the core region, there is a large difference. The errors of SSPH are mainly caused by this difficulty.

4. Summary
We presented SSPH as one of the discretization techniques in real-space electronic structure calculations. SSPH was applied to real-space electronic structure calculations of a simple atom such as hydrogen, helium and lithium. The accuracy was similar to that of FD. If the number of the particles of SSPH is enough to describe the steep change of the field function, SSPH provides the fairly good accuracy. Our results indicate that SSPH can be applicable to the electronic structure calculations that require high accuracy.

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