

Non-orthogonal basis adapted parameter-free complex absorbing potential and its application to open-boundary cluster model

Kosuke Imamura,¹ Tomokazu Yasuike,² and Hirofumi Sato^{*1,3}

¹Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

²Department of Liberal Arts, Faculty of Liberal Arts, The Open University of Japan, Chiba, 261-8586, Japan

³Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan

* Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

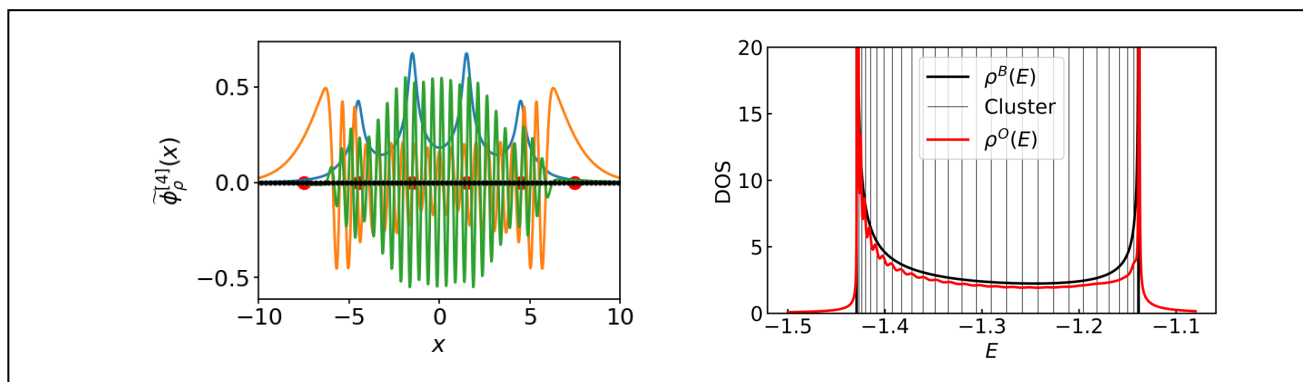
Email: hirofumi@moleng.kyoto-u.ac.jp

Abstract

This study extends the method of determining the complex absorbing potential (CAP) required for the open-boundary cluster model (OCM) based on the surface Green's function theory [*J. Chem. Phys.* **2024**, *160*, 034103] to allow calculations using non-orthogonal basis sets. We devised a novel scheme that avoids the need to find adiabatically connected solutions for a large number of virtual energy levels, caused by the basis set expansion, and succeeded in constructing an optimal CAP. We generated basis sets with plane wave-like characteristics solely from localized functions, thereby eliminating the numerical instability in calculations of the surface Green's function. Application of the obtained CAP to the OCM calculation of a model one-dimensional system confirms that the DOS of solid and localized states is well reproduced.

Keywords: Cluster model, surface, complex absorbing potential

Graphical abstract



1. Introduction

Cluster model is the simplest approach for treating heterogeneous systems, such as surface and lattice defects, with quantum chemistry.^{1,2} In this model, quantum chemical calculations are performed on the heterogeneous structure and its surrounding solid atoms. However, the effects of solids cannot be adequately described, and edge effects can no longer be ignored when the size of the substrate is small. While this problem can sometimes be circumvented by computing large clusters,^{3,4} it is common to employ embedded models that simulate the effects of the surrounding solids.^{1,5,6,7} These methods share the idea of embedding clusters in the solid environment.

Yasuike and Nobusada have devised another method that incorporates the effect of solids into the cluster model, referred to as the open-boundary cluster model (OCM).^{8,9} The main idea of OCM is to perform cluster calculations under the outgoing-wave boundary condition. With this boundary condition, energy eigenvalues become complex values with negative imaginary parts. In other words, each electronic state is modeled as a resonance (Siebert) state.¹⁰ This mimics the spread of electrons out of the cluster, which is neglected in conventional cluster model. In the early applications of OCM, the complex scaling method is utilized to impose the boundary condition.^{11,12} As another method, we can use complex absorbing potentials (CAPs) for it.^{12,13} Quantum chemical calculations with CAPs are easier than complex scaling because we

only have to add complex-valued potentials into the system. This is nearly the same cost as the conventional cluster model; the only differences exist in matrix operation from real symmetric to complex symmetric. If an appropriate CAP can be prepared, OCM calculations using CAP are expected to be the least computationally intensive in terms of incorporating solid effects into the cluster model. Additionally, accumulations of quantum chemical theory to date can be used, and recent theoretical developments are significant. OCM calculations have been applied to a variety of model and actual systems, and their effectiveness for describing surface phenomena has been demonstrated.^{8,9,14,15,16} Textbooks on non-Hermitian quantum mechanics may be helpful for understanding the concepts of CAP and OCM in detail.^{17,18}

Recently, we proposed a novel method for constructing a CAP¹⁹ based on the electron self-energy.²⁰ This CAP is free from parameter optimization, avoiding the use of the complex variational principle.²¹ While the physical meaning of the complex variational principle is unclear, the newly proposed CAP is based on surface Green's function theory. Another advantage is that the CAP is band-specifically determined. In the previous study,¹⁹ the parameter-free CAP was applied to a simple tight-binding model and successfully described the surface states of a semi-infinite one-dimensional chain. This clarified the connection between OCM and surface Green's function theory. However, the tight-binding Hamiltonian was constructed without explicit basis functions in the study. In an application of this approach to realistic quantum chemical calculations, an extension to non-orthogonal basis sets is required. It is noted that the previous OCM calculations were performed with discrete variable representation^{8,14,15} or grid basis sets,^{9,16} and this is the first attempt to perform OCM calculations with non-orthogonal basis functions.

In this study, we extend the parameter-free CAP proposed in the previous study¹⁹ to OCM calculations with non-orthogonal basis functions. The theoretical details are presented in Sec. 2. The parameter settings and other calculation conditions are summarized in Sec. 3. In Sec. 4, the construction of basis sets and CAPs is shown, and the OCM calculations for localized states near a band are carried out. Finally, the conclusion of this study is presented.

2. Theory

In this study, we consider the following Hamiltonian describing a model one-dimensional system

$$\left\{ -\frac{1}{2} \frac{d^2}{dx^2} + V(x) \right\} \Psi(x) = E \Psi(x), \quad (1)$$

$$V(x) = - \sum_{k=1}^N \frac{D_k}{\cosh^2(x - R_k)}, \quad (2)$$

$$R_k = \left(k - \frac{N+1}{2} \right) a. \quad (3)$$

The potential $V(x)$ has N minima whose intervals are a , and depths are controlled by D_k . We assume that atoms exist in these minima, referred to as sites with indices k or l .

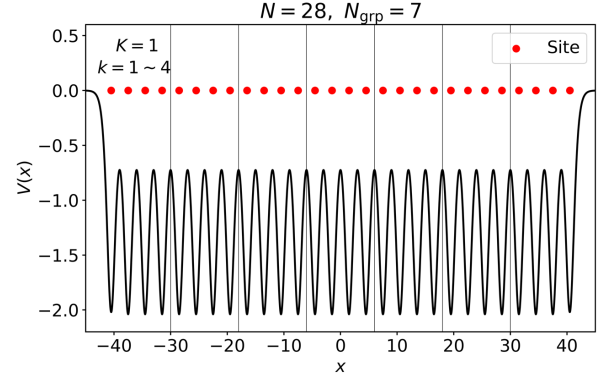


Fig. 1. The form of potential function in Eq. (1) when $N = 28$ and $N_{\text{grp}} = 7$. The site positions are shown in red circles, whose intervals a are set to 3.0. In this figure, the depths D_k are all the same, 2.0.

We employ s -type Gaussian basis functions for solving Eq. (1)

$$\phi_{\mu}^{(k)} = \left(\frac{2\alpha_{\mu}}{\pi} \right)^{\frac{1}{4}} e^{-\alpha_{\mu}(x-R_k)^2} \quad (\mu \in k), \quad (4)$$

and the resulting eigenvalue problem is expressed by

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon, \quad (5)$$

where $\mathbf{C}$ is the coefficient matrix. To apply the surface Green's function method, the Hamiltonian matrix $\mathbf{H}$ and overlap matrix $\mathbf{S}$ should be symmetric Toeplitz matrices. However, since the Gaussian function with a small exponent spreads over the site interval a , significant truncation occurs when the site is chosen as the repeating unit. We therefore define a group consisting of N_{gs} sites as the repeating unit. The number of groups N_{grp} is given by $N_{\text{grp}} = N/N_{\text{gs}}$, with indices denoted as K or L . The component of the overlap matrix between two groups is

$$(\mathbf{S}^{[K,L]})_{k\mu,l\nu} = \langle \phi_{\mu}^{(k)} | \phi_{\nu}^{(l)} \rangle \quad (k \in K, l \in L). \quad (6)$$

It is noted that square brackets are used to specify a group. In this study, N_{gs} is selected so that the elements of $\mathbf{H}^{[K,L]}$ and $\mathbf{S}^{[K,L]}$ are sufficiently small for $|K - L| \geq 2$.

The linear dependencies in the Gaussian functions make the evaluation of the self-energy matrix [Eq. (15)], which is required for constructing the CAP, difficult due to inverse instability. We eliminated this issue for each group using the canonical orthogonalization method.²² The eigenvalue of the overlap matrix within the same group K is given by

$$\mathbf{S}^{[K,K]} \mathbf{R}^{[K,K]} = \mathbf{R}^{[K,K]} \mathbf{S}^{[K,K]}, \quad (7)$$

and the transformation matrix $\mathbf{X}^{[K,K]}$ is defined as follows:

$$\mathbf{X}^{[K,K]} = \mathbf{R}^{[K,K]} \left(\mathbf{s}_t^{[K,K]} \right)^{-\frac{1}{2}}. \quad (8)$$

In this equation, the truncated eigenvalue matrix $\mathbf{s}_t^{[K,K]}$ is

$$\mathbf{s}_t^{[K,K]} = \text{diag} \left(s_1^{[K,K]}, \dots, s_{\tilde{M}}^{[K,K]}, 0, \dots, 0 \right), \quad (9)$$

where eigenvalues are sorted in descending order and eigenvalues smaller than a threshold are approximated as 0. $\tilde{M}$ represents the number of basis functions in each group after truncation, and the tilde symbol is placed on quantities associated with truncated basis functions. Consequently, the transformed basis function is written by

$$\tilde{\phi}_\rho^{[K]}(x) = \sum_{k \in K} \sum_{\mu \in k} X_{k\mu,\rho}^{[K,K]} \phi_\mu^{(k)}(x) \quad (\rho = 1, \dots, \tilde{M}), \quad (10)$$

and the corresponding Hamiltonian and overlap matrices are

$$\tilde{\mathbf{H}}^{[K,L]} = [\mathbf{X}^{[K,K]}]^\dagger \mathbf{H}^{[K,L]} \mathbf{X}^{[L,L]}, \quad (11)$$

$$\tilde{\mathbf{S}}^{[K,L]} = [\mathbf{X}^{[K,K]}]^\dagger \mathbf{S}^{[K,L]} \mathbf{X}^{[L,L]}. \quad (12)$$

For example, the component of the overlap matrix is

$$(\tilde{\mathbf{S}}^{[K,L]})_{\rho\sigma} = \langle \tilde{\phi}_\rho^{[K]} | \tilde{\phi}_\sigma^{[L]} \rangle, \quad (13)$$

which equals to $\delta_{\rho\sigma}$ when $K = L$.

The self-energy for the right electrode is denoted by $\tilde{\sigma}(\epsilon)$ and that for the left electrode is denoted by $\tilde{\sigma}(\epsilon)$. $\tilde{\sigma}(\epsilon)$ is numerically computed with $\tilde{\mathbf{Q}}^{[-2,-2]}$ and $\tilde{\mathbf{Q}}^{[-2,-1]}$ as inputs ($\mathbf{Q} = \mathbf{H}, \mathbf{S}$), and $\tilde{\sigma}(\epsilon)$ is also computed with a slightly different scheme using the same inputs.²³ Here, the negative index $-n$ represents the $(N_{\text{grp}} - n + 1)$ -th group. To construct a CAP, we solve Dyson's equation for an infinite chain

$$[\tilde{\mathbf{H}} + \tilde{\Sigma}(\epsilon)] \mathbf{U} = \epsilon \tilde{\mathbf{S}} \mathbf{U}. \quad (14)$$

We omit the equation for the left vector $\mathbf{V}^\dagger$ here. The matrix $\tilde{\Sigma}$ is defined as follows:

$$\tilde{\Sigma}(E + i\delta) = \begin{bmatrix} \tilde{\sigma}(E + i\delta) & \mathbf{0} & \cdots & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \cdots & \mathbf{0} & \mathbf{0} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \mathbf{0} & \mathbf{0} & \cdots & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \cdots & \mathbf{0} & \tilde{\sigma}(E + i\delta) \end{bmatrix}. \quad (15)$$

Density of states (DOS) is computed from the following equation

$$\rho^G(E) = -\frac{1}{N_A} \frac{1}{2i\pi} \text{tr} [\tilde{\mathbf{S}} \{ \mathbf{G}(E) - \mathbf{G}^\dagger(E) \}], \quad (16)$$

where Green's matrix is defined as²⁴

$$\mathbf{G}(E) = \{ (E + i\delta) \tilde{\mathbf{S}} - \tilde{\mathbf{H}} + \tilde{\Sigma}(E + i\delta) \}^{-1}. \quad (17)$$

N_A is the number of adiabatically connected eigenstates, which can be taken as equal to the number of sites N when we are interested in the lowest energy band. This DOS computed from Green's matrix is regarded as exact when the matrix size is sufficiently large.

Once the solution to Eq. (14) is obtained, we can construct a symmetrized CAP based on the scheme from a previous study.¹⁹ Namely, after solving the following equations in the p -th iteration

$$[\tilde{\mathbf{H}} + \tilde{\mathbf{W}}^p] \mathbf{U}^{p+1} = \tilde{\mathbf{S}} \mathbf{U}^{p+1} \epsilon^{p+1}, \quad (18)$$

$$(\mathbf{V}^{p+1})^\dagger [\tilde{\mathbf{H}} + \tilde{\mathbf{W}}^p] = \epsilon^{p+1} (\mathbf{V}^{p+1})^\dagger \tilde{\mathbf{S}}, \quad (19)$$

with

$$\tilde{\mathbf{W}}^p = \frac{\mathbf{W}_R^p + \mathbf{W}_L^p}{2}, \quad (20)$$

we update the next step CAPs as^{19,25}

$$\mathbf{W}_R^{p+1} = \tilde{\mathbf{S}} \mathbf{U}^{p+1} \epsilon^1 (\mathbf{U}^{p+1})^{-1} - \tilde{\mathbf{H}}, \quad (21)$$

$$\mathbf{W}_L^{p+1} = \{ (\mathbf{V}^{p+1})^\dagger \}^{-1} \epsilon^1 (\mathbf{V}^{p+1})^\dagger \tilde{\mathbf{S}} - \tilde{\mathbf{H}}. \quad (22)$$

As in the previous study, we use ϵ^1 for updating CAPs. The initial eigenvalue matrix ϵ^1 and vectors $\mathbf{U}^1, \mathbf{V}^1$ are obtained from the adiabatically connected solutions to Eq. (14).

Special consideration is needed when using the basis set expansion. Many states appear as the number of basis sets increases, but it is not realistic to solve Eq. (14) for all of them. Since we are only interested in several bands in many cases, it is useful to limit the number of eigenstates, which is written as N_A . In this case, however, the inverses in Eqs. (21) and (22) are not defined because $\mathbf{U}, \mathbf{V}^\dagger$ are not square matrices. We circumvent this problem by approximating the remaining states with localized states of the cluster Hamiltonian given by

$$\tilde{\mathbf{H}}\mathbf{T}^c = \tilde{\mathbf{S}}\mathbf{T}^c\epsilon^c. \quad (23)$$

With the use of this solution, the square matrices are constructed as follows:

$$\mathbf{U}^{p+1} \leftarrow (\mathbf{u}_1^{p+1}, \dots, \mathbf{u}_{N_A}^{p+1}, \mathbf{t}_{N_A+1}^c, \dots, \mathbf{t}_{M_{N_{\text{grp}}}}^c), \quad (24)$$

$$\mathbf{V}^{p+1} \leftarrow (\mathbf{v}_1^{p+1}, \dots, \mathbf{v}_{N_A}^{p+1}, \mathbf{t}_{N_A+1}^c, \dots, \mathbf{t}_{M_{N_{\text{grp}}}}^c), \quad (25)$$

$$\epsilon^1 \leftarrow \text{diag}(\epsilon_1^1, \dots, \epsilon_{N_A}^1, \epsilon_{N_A+1}^c, \dots, \epsilon_{M_{N_{\text{grp}}}}^c). \quad (26)$$

In Eqs. (24) to (26), the eigenvalues and eigenvectors are sorted so that the real part of the eigenvalues are in ascending order. This approximation implies that, for states above the band of interest, we use solutions for a finite-sized cluster. This approach will not cause difficulties in this study, as we focused only on the occupied band and the band gap is large. However, this approach is considered insufficient for the calculation of excited states.

This approach allows us to obtain complex energies for the physically-relevant N_A orbitals, which can then be used to describe the continuous density of states (see also Eq. (28) below). In the present model, N_A should be set equal to the number of sites N if we are interested in the occupied band. If the conduction band just above it is composed of N orbitals, $N_A = 2N$ can be used when considering both occupied and conduction bands. After the construction of a CAP, OCM calculations are performed as follows:

$$[\tilde{\mathbf{H}} + \bar{\mathbf{W}}^{\text{opt}}]\mathbf{u}_m = (\omega_m - i\gamma_m)\tilde{\mathbf{S}}\mathbf{u}_m, \quad (27)$$

where ω_m/γ_m represents the real/imaginary part of the complex eigenvalue, respectively. $\bar{\mathbf{W}}^{\text{opt}}$ is obtained as $\bar{\mathbf{W}}^p$ at the value of p for which Eqs. (20) through (22) become self-consistent. The DOS from the OCM calculation, denoted as $\rho^o(E)$, is expressed by

$$\rho^o(E) = \frac{1}{N_A} \frac{1}{\pi} \sum_{m=1}^{N_A} \frac{\gamma_m}{(E - \omega_m)^2 + \gamma_m^2}, \quad (28)$$

which is the superposition of Lorentz functions.

There are several studies that analyze molecular electronics junctions using a tight-binding model with non-orthogonal basis sets.^{26,27} Compared to these studies, our approach has the advantage that it does not require integration in continuous energy space. For example, the DOS is analytically expressed using complex eigenvalues as in Eq. (28), rather than as energy integrals of Green's function. However, it seems necessary to find adiabatically connected solutions for a large number of virtual orbitals when adopting non-orthogonal basis sets, which differs from the previous report.¹⁹ The present study avoids this

issue based on the approximation in Eqs. (23) — (26) and is formulated to allow for consistent discussions with molecular orbitals.

3. Computational details

We set the total number of sites N to 28, and the interval a is set to 3.0. We define seven groups, each comprising four sites, resulting in $N_{\text{grp}} = 7$ and $N_{\text{gs}} = 4$. The depths of each site D_k are initially set to 2.0, and these values are slightly modified in Sec. 4 C. The exact DOS with these parameter sets $[\rho^B(E)]$ was computed through a band calculation, and further details can be found in Ref. 8. In this study, we focused solely on the lowest band, and we solve Eq. (14) for the 28 lowest eigenstates ($N_A = 28$). The imaginary shift δ is chosen to be 1.0×10^{-4} . Adiabatically connected states are calculated using the same procedure as shown in Ref. 19. The evaluation of kinetic and overlap integrals is performed analytically, while the integrals with potential $V(x)$ are computed numerically. The grid points are placed in the range of $x = -80$ to $x = 80$ with an interval of 0.02.

4. Results and discussion

4. A. Preparation of basis sets

First, we present the details of basis set construction. The number of Gaussian basis functions on each site, denoted as N_b , is set to 13, and their exponents are

$$\alpha_\mu = 0.1, 0.2, 0.3, 0.5, 0.7, 1.0, 1.5, 2.5, 4.0, 7.0, 10.0, 20.0, 30.0. \quad (29)$$

Additionally, we augment off-site functions to generate plane-wave-like basis sets. This leads to a natural description for the system where discrete and continuous electronic structure coexist. The exponents and positions of the Gaussian functions are set as follows:²⁸

$$\alpha_\mu = \frac{16}{\eta^2}, \quad (30)$$

$$R_\mu = R_k + \frac{\eta}{4} \left(n - \frac{1}{2} \right) \quad (\mu \in k). \quad (31)$$

These functions allow the expression of plane waves with a minimum wavelength of up to $\eta/2$. In this study, the value of η is determined by

$$\eta = \frac{4a}{N_p}, \quad (32)$$

and the N_p Gaussian functions are positioned at $n = -N_p/2, -N_p/2 + 1, \dots, N_p/2$. In this study, N_p was set to 12 to ensure that it is a multiple of N_{gs} . The total number of basis functions in each group $\{\tilde{\phi}_\rho^{[K]}(x)\}$, calculated as $N_{\text{gs}}(N_b + N_p)$, is 100 in this case.

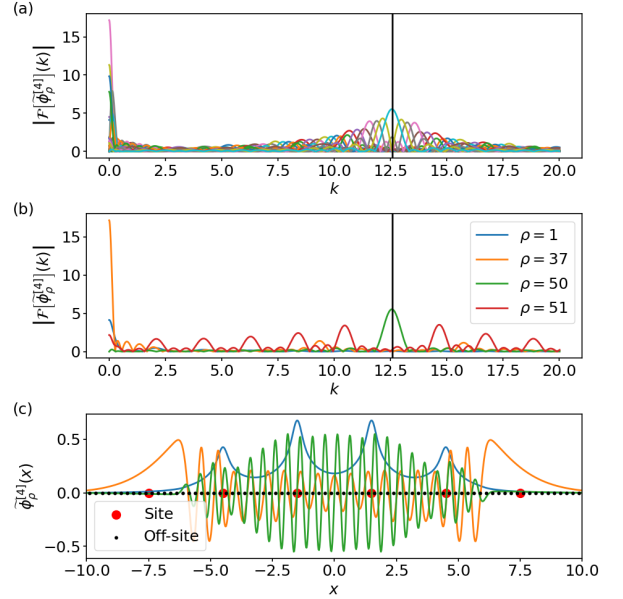
1 To validate the basis sets transformed as Eq. (10), we
 2 computed the Fourier transforms of the generated
 3 basis functions

$$\begin{aligned}
 4 \quad \mathcal{F}[\tilde{\phi}_\rho^{[K]}](k) &= \sum_{l \in K} \sum_{\mu \in l} X_{l\mu,\rho}^{[K,K]} \int dx \phi_\mu^{(l)}(x) e^{-ikx}, \\
 5 \quad &= \sum_{l \in K} \sum_{\mu \in l} \frac{\sqrt{\pi}}{\alpha_\mu} X_{l\mu,\rho}^{[K,K]} e^{-ikR_K} e^{-\frac{k^2}{4\alpha_\mu^2}}. \quad (33)
 \end{aligned}$$

6 While the Fourier transform of a single Gaussian
 7 function has a peak around $k = 0$, a generated basis
 8 function with plane-wave-like characteristics should
 9 exhibit a peak corresponding to the momentum of the
 10 plane wave. **Fig. 2** (a) displays the absolute values of the
 11 Fourier transforms for 50 basis functions with large
 12 eigenvalues in Eq. (9) for the fourth group. The black
 13 vertical line in the figure corresponds to the momentum
 14 $k_{\max} = 2\pi/(\eta/2)$, which represents the maximum
 15 momentum (or minimum wavelength). The Fourier
 16 transforms for the 50th and 51st basis functions are
 17 also shown in **Fig. 2** (b). The result for $\rho = 50$ shows a
 18 sharp peak around the vertical black line. This basis
 19 function appears to exhibit characteristics resembling
 20 those of a plane wave with a minimum wavelength. On
 21 the other hand, the Fourier transform for the 51st basis
 22 function shows multiple peaks. Additionally, the
 23 momentum space (k -space) is well covered by 50
 24 functions in **Fig. 2** (a), and adding the 51st basis would
 25 likely result in an increase in linear dependence.
 26 Therefore, we set the total number of basis functions
 27 in each group $\tilde{M}$ to 50 in this study, where the
 28 threshold for truncation is 3.5×10^{-2} . In other words, the
 29 number of basis functions used in the present
 30 calculation is 350, and to evaluate Eqs. (21) and (22)
 31 without approximation, it is necessary to find
 32 adiabatically connected solutions for all of them.
 33 However, with the approach introduced in Eqs. (23)
 34 through (26), we only need such solutions for the
 35 lowest 28 energy levels, leading to a significant
 36 reduction in computational cost.

37
 38 Fourier transforms for selected functions are shown in
 39 **Fig. 2** (b), and the real space representations, except for
 40 $\rho = 51$, are depicted in **Fig. 2** (c). The Fourier transform
 41 of $\tilde{\phi}_1^{[4]}(x)$ exhibits a prominent peak around $k=0$, and
 42 the basis function is localized near the four sites.
 43 Conversely, $\tilde{\phi}_{50}^{[4]}(k)$ shows a characteristic peak around
 44 $k = k_{\max}$. $\tilde{\phi}_{50}^{[4]}(x)$ exhibits plane-wave-like properties
 45 with beat structures.

46 Thus, this basis construction has a similar effect to the
 47 cutoff in k -space. The highest peak around $k = 0$
 48 corresponds to $\tilde{\phi}_{37}^{[4]}(x)$. This basis function
 49 demonstrates plane-wave-like characteristics in the
 50 center of the group and localized behavior around the
 51 edges of the group. This behavior appears to play an
 52 important role in describing the coupling with the
 53 neighboring groups. In this way, we succeeded in
 54 constructing basis sets that reflect both localized and
 55 delocalized natures.



56 **Fig. 2.** (a) Plot of the Fourier transform of the generated
 57 basis functions $\{\tilde{\phi}_\rho^{[4]}(x)\}$. Among the 100 basis
 58 functions, 50 functions with the largest eigenvalues are
 59 shown. (b) Selected plots of four basis functions $\rho =$
 60 1, 37, 50, 51 from (a). (c) Real space representations of
 61 selected basis functions $\rho = 1, 37, 50$. Red points
 62 indicate the positions of each site, and black points
 63 denote the positions of off-site Gaussian functions.

64

65 4. B. Construction of CAP

66

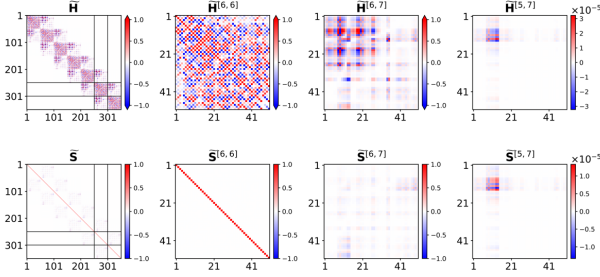
67 Before constructing a CAP, we verified that the
 68 Hamiltonian and overlap matrices with the generated
 69 basis functions are indeed Toeplitz matrices. The
 70 components of the Hamiltonian and overlap matrices
 71 are shown in **Fig. 3**. Due to its construction, $\tilde{\mathbf{S}}^{[6,6]}$ is the
 72 identity matrix. Interestingly, $\tilde{\mathbf{S}}^{[6,7]}$ has only small
 73 components, resulting in the total overlap matrix being
 74 like the identity matrix. Additionally, the [5,7] block is
 75 almost a zero matrix for both the Hamiltonian and
 76 overlap matrices. Therefore, N_{gs} is sufficiently large,
 77 and the approximation for calculating the self-energy
 78 matrix is valid.

78

1 We solved the Dyson equation with the generated
 2 basis sets and constructed a CAP using the procedure
 3 described above. As many elements of the CAP matrix
 4 have small values, a matrix representing the density of
 5 effective elements was defined and calculated as
 6 follows:

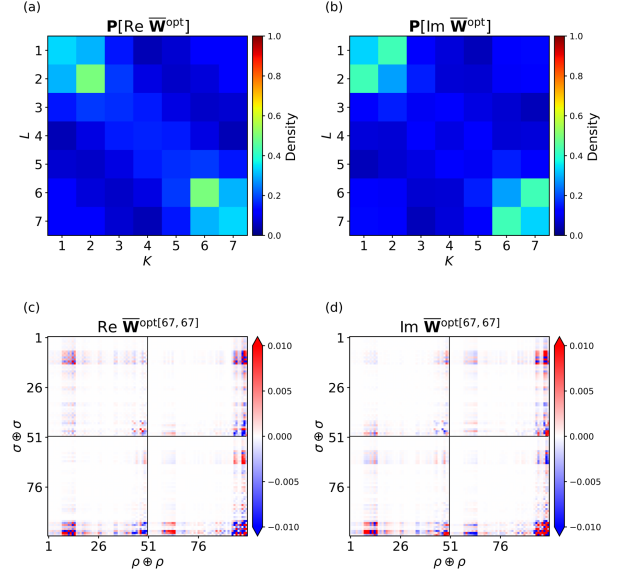
$$7 \quad P_{KL}[\mathbf{W}] = \frac{1}{M} \sum_{\rho\sigma} H_{\theta} \left(W_{\rho\sigma}^{[K,L]} - 1.0 \times 10^{-4} \right), \quad (34)$$

8 where $H_{\theta}(x)$ is the Heaviside step function. The
 9 components of the density matrix $\mathbf{P}$ for the real and
 10 imaginary parts are shown in **Fig. 4** (a) and (b),
 11 respectively. The large density is observed near the
 12 corner connected to the right/left electrodes.
 13 Conversely, the remaining blocks are occupied by
 14 smaller components. The localization of CAP in the
 15 neighborhood connected to the electrodes is
 16 consistent with the behavior observed in the previous
 17 study.¹⁹ The components of $\bar{\mathbf{W}}^{\text{opt}}$ limited to the 2x2
 18 blocks are shown in **Fig. 4** (c) and (d). The largest
 19 components are in the lower-right block for both the
 20 real and imaginary parts. It can be observed that the
 21 CAP is indeed symmetric. These results indicate the
 22 successful construction of the CAP.



23 **Fig. 3.** Components of the Hamiltonian matrix (top
 24 panels) and overlap matrix (bottom panels) are
 25 displayed. Enlarged views of $\bar{\mathbf{Q}}^{[6,6]}$ and $\bar{\mathbf{Q}}^{[6,7]}$ are
 26 shown, which are the inputs for calculating the
 27 self-energy matrix ($\mathbf{Q} = \mathbf{H}, \mathbf{S}$). The [5,7] blocks are
 28 also displayed to confirm that they indeed have
 29 small components.

30



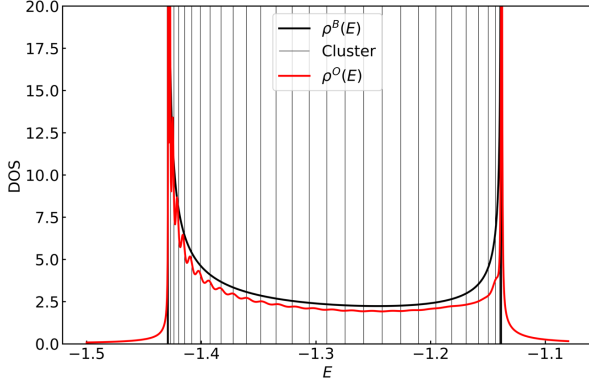
31 **Fig. 4.** The density of effective elements in the
 32 real part (a) and the imaginary part (b) of the
 33 constructed CAP. (c), (d) The enlarged views of
 34 the [67,67] blocks of the constructed CAP,
 35 separately presented for the real and imaginary
 36 parts.

37

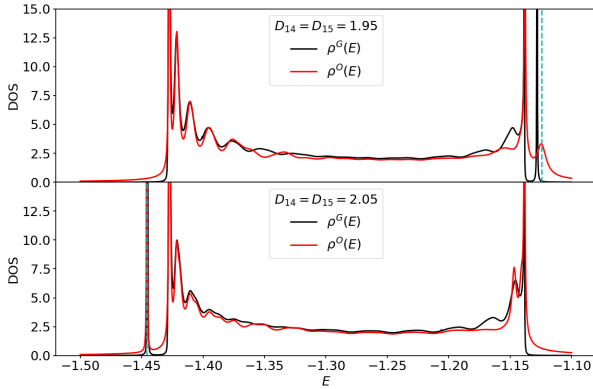
38 4. C. OCM calculations

39 We then perform an OCM calculation for an infinite
 40 chain. In this case, all sites have the same depth,
 41 indicating that we are calculating pure solids. In **Fig. 5**,
 42 we compare the DOS from the OCM calculation, $\rho^O(E)$,
 43 with the exact DOS, $\rho^B(E)$. Additionally, we present
 44 the discrete energy levels of the cluster model. The
 45 shape of the exact DOS in black is well approximated
 46 by the superposition of Lorentz functions in red. We
 47 thus confirmed the effectiveness of determining the
 48 CAP to ensure that the resonance states in the OCM
 49 calculation reproduce the solutions of the Dyson
 50 equation, even when using non-orthogonal basis sets.
 51 While there is more smearing at the band edges
 52 compared to what was observed in the previously
 53 applied tight-binding model,¹⁹ we believe that this can
 54 be improved by increasing the number of total sites N .
 55 Generally, increasing the number of sites, i.e., the
 56 number of states contributing to a single band,
 57 improves the resolution of the DOS. However, this
 58 enhancement comes with increased computational
 59 cost, presenting a tradeoff. The results of slight
 60 changes N_{gs} and N_{grp} are summarized in Figs. S1
 61 through S3. There is only a slight improvement in the
 62 rise of the DOS in the higher energy region. It can be
 63 observed that the parameters N_{gs} and N_{grp} can be

1 freely chosen as long as the cluster size is sufficiently
 2 large. It may also be necessary to significantly increase
 3 the cluster size to improve the resolution of the DOS.



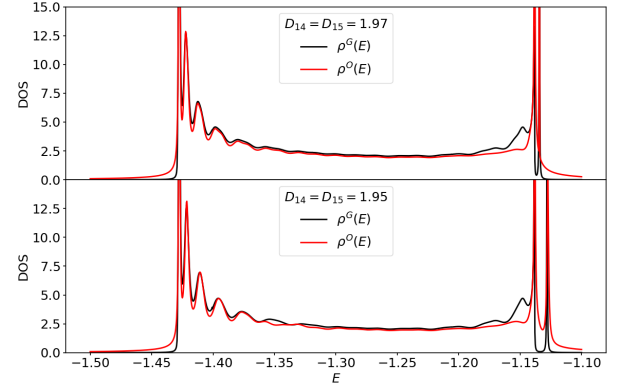
4 **Fig. 5.** The comparison of $\rho^B(E)$ and $\rho^O(E)$ is
 5 shown. The exact DOS is represented by the solid
 6 black line. The DOS of the cluster is depicted by
 7 the thin black lines. The red line from the OCM
 8 calculation well reproduces the shape of the exact
 9 result.



10 **Fig. 6.** Computed DOS from OCM calculations with
 11 the optimized CAP for the pure solid (red) and
 12 those from Green's matrix (black). The cluster
 13 Hamiltonian is slightly modified to generate a
 14 localized state by adjusting the depth parameters
 15 D_{14} and D_{15} . The vertical dashed line represents
 16 the real part of the energy eigenvalue of the
 17 localized state. The upper panel shows the results
 18 for $D_{14} = D_{15} = 1.95$, while the lower panel shows
 19 the results for $D_{14} = D_{15} = 2.05$.

20

21 The constructed CAP for the pure solid is also used for
 22 calculating localized states near the band edges. To
 23 simulate this, we set the depth parameters for the two
 24 central sites, specifically D_{14} and D_{15} , to either 1.95 or
 25 2.05. We then reused the CAP originally constructed for
 26 the pure solid. The computed DOSs with OCM
 27 calculations and Green's functions are compared in **Fig.**
 28 **6.** For localized states, the real parts of the
 29 corresponding complex eigenvalues are indicated by
 30 vertical dashed lines. The DOSs in the band region are
 31 well described in both the top and bottom panels,
 32 including several newly produced peak structures.
 33 When we set D_{14} and D_{15} to 1.95, the peak position of
 34 the localized state in the OCM calculation is shifted a
 35 little, and its width is overestimated. In the bottom plot
 36 ($D_{14} = D_{15} = 2.05$), the peak position and width are
 37 correct. We think that this difference is related to the
 38 fact that the cluster model has more energy levels on
 39 the lower energy side, i.e., the DOS resolution is higher
 40 at the lower energy side.



41 **Fig. 7.** Computed DOS from OCM calculations with
 42 the optimized CAP for the pure solid (red) and
 43 those from Green's matrix (black). The cluster
 44 Hamiltonian is slightly modified to generate a
 45 localized state by adjusting the depth parameters
 46 D_{14} and D_{15} .

47 The above problem can be attributed to using an
 48 improper reference. We thus constructed another CAP
 49 by setting $D_{14} = D_{15} = 1.97$ and then reused it to
 50 describe the system with $D_{14} = D_{15} = 1.95$. In the top
 51 panel of **Fig. 7**, we display the DOS for $D_{14} = D_{15} = 1.97$.
 52 In this case, the CAP used in the OCM calculation is
 53 derived from the adiabatically connected states with
 54 $D_{14} = D_{15} = 1.97$. This effectively describes both the
 55 band region and the localized state. In the bottom plot
 56 of **Fig. 7**, only the Hamiltonian is changed, and the
 57 constructed CAP is used for the OCM calculation. In
 58 this case, the localized state near $E = -1.13$ is better
 59 described compared to **Fig. 6**. This indicates the
 60 importance of constructing the CAP using adiabatically
 61

connected solutions for the reference system close to the system of interest.

Finally, we compared the energy of the impurity level that appears on the higher energy side. For $D_{14} = D_{15} = 1.97$, the energy calculated using Green's function theory is $E = -1.135$, and that of the OCM calculation is $E = -1.134$. The latter value is obtained from the real part of the complex eigenvalue regarding the impurity level. Similarly, the energy difference is small for $D_{14} = D_{15} = 1.95$, with Green's function theory yielding $E = -1.128$ and the OCM calculation yielding $E = -1.127$. Thus, impurity levels are expected to be predictable using a CAP constructed for an appropriate reference system.

5. Conclusion

In this study, we proposed a novel scheme for constructing a CAP with non-orthogonal basis sets and applied the CAP to OCM calculations. By defining groups larger than the spread of the Gaussian functions, we can calculate the self-energy matrix while keeping the truncation error small. By placing basis functions periodically at off-site locations, we constructed basis functions with localized nature and those with plane-wave-like character to coexist. The number of basis functions can be determined by using the Fourier transform of the obtained basis functions. This provides an effect similar to performing a cutoff in k -space. The CAPs constructed by the proposed method localized their values at the junctions with the electrodes, as observed in the previous study.¹⁹ The OCM calculation with the obtained CAP well reproduced the exact DOS of a one-dimensional pure solid well. We investigated whether the CAP obtained for the pure solid is also applicable to cases where localized states occur. In cases where a localized state occurs at lower energies, the reuse of the CAP was valid. The description of the localized states on the high-energy side was not satisfactory when the reference system was the pure solid, but by taking a different reference system, the shape of the DOS was well reproduced. This suggests that it is important to choose an appropriate reference system when constructing the CAP. The results of this study are expected to facilitate OCM calculations in combination with quantum chemistry programs.

Acknowledgement

K.I. thanks the Grant-in-Aid for the Japan Society for Promotion of Science (JSPS) Fellows. Theoretical computations were partly performed using Research Center for Computational Science, Okazaki, Japan (Project: 23-IMS-C017).

Funding

This work was supported by JSPS KAKENHI (Grant Nos. JP21J21500 and JP23H01922).

References

- 1 J. Weber, J. S. auf der G nne, *Phys. Chem. Chem. Phys.* **2010**, *12*, 583.
- 2 O. T. Hofmann, E. Zojer, L. H rmann, A. Jeindl, R. J. Maurer, *Phys. Chem. Chem. Phys.* **2021**, *23*, 8132.
- 3 J. Larsson, P. Delaney, *Phys. Rev. B* **2008**, *77*, 165201.
- 4 C.-K. Lin, Y.-H. Wang, H.-C. Chang, M. Hayashi, S. Lin, *J. Chem. Phys.* **2008**, *129*, 124714.
- 5 G. A. Bramley, O. T. Beynon, P. V. Stishenko, A. J. Logsdail, *Phys. Chem. Chem. Phys.* **2023**, *25*, 6562.
- 6 Q. Sun, G. K.-L. Chan, *Acc. Chem. Res.* **2016**, *49*, 2705.
- 7 L. O. Jones, M. A. Mosquera, G. C. Schatz, M. A. Ratner, *J. Am. Chem. Soc.* **2020**, *142*, 3281.
- 8 T. Yasuike, K. Nobusada, *Phys. Rev. B* **2007**, *76*, 235401.
- 9 T. Yasuike, K. Nobusada, *Phys. Rev. B* **2011**, *84*, 245408.
- 10 A. J. Siegert, *Phys. Rev.* **1939**, *56*, 750.
- 11 N. Moiseyev, *Phys. Rep.* **1998**, *302*, 212.
- 12 T.-C. Jagau, K. B. Bravaya, A. I. Krylov, *Ann. Rev. Phys. Chem.* **2017**, *68*, 525.
- 13 U. V. Riss, H.-D. Meyer, *J. Phys. B: At., Mol. Opt. Phys.* **1993**, *26*, 4503.
- 14 T. Yasuike, K. Nobusada, *Chem. Phys. Lett.* **2008**, *457*, 241.
- 15 T. Yasuike, K. Nobusada, *Phys. Rev. B* **2009**, *80*, 035430.
- 16 K. Iida, T. Yasuike, K. Nobusada, *J. Chem. Phys.* **2013**, *139*, 104101.
- 17 *Non-Hermitian Quantum Mechanics*, ed. by N. Moiseyev, Cambridge University Press, Cambridge, **2011**.
- 18 *Non-Hermitian Quantum Mechanics*, ed. by N. Hatano, K.-I. Imura, Kodansha Scientific, Tokyo, **2023**.
- 19 K. Imamura, T. Yasuike, H. Sato, *J. Chem. Phys.* **2024**, *160*, 034103.
- 20 T. M. Henderson, G. Fagas, E. Hyde, J. C. Greer, *J. Chem. Phys.* **2006**, *125*, 244104.
- 21 N. Moiseyev, P. R. Certain, F. Weinhold, *Mol. Phys.* **1978**, *36*, 1613.
- 22 A. Szabo, N. S. Ostlund, in *Modern quantum chemistry: introduction to advanced electronic structure theory*, Courier Corporation, **2012**.
- 23 M. P. L. Sancho, J. M. L. Sancho, and J. Rubio, *J. Phys. F: Met. Phys.* **1985**, *15*, 851.
- 24 S. Priyadarshy, S. S. Skourtis, S. M. Risser, D. N. Beratan, *J. Chem. Phys.* **1996**, *104*, 9473.
- 25 M. Szeplieniec, I. Yeriskin, J. C. Greer, *J. Chem. Phys.* **2013**, *138*, 144105.
- 26 O. Hod, J. E. Peralta, G. E. Scuseria, *J. Chem. Phys.* **2006**, *125*, 114704.
- 27 A. Prociuk, B. Van Kuiken, B. D. Dunietz, *J. Chem. Phys.* **2006**, *125*, 204717.
- 28 T. Yasuike, K. Someda, *Phys. Rev. A* **2008**, *78*, 013403.

