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Link molecule method for quantum mechanical/molecular mechanical hybrid simulations

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Abstract

We present a new coupling method for hybrid simulations in which the system is partitioned into covalently linked quantum mechanical (QM) and molecular mechanical (MM) regions. Our method, called the "link molecule method (LMM)," is substantially different from the link atom methods in that LMM is free from the delicate issue of how to remove the additional degrees of freedom with respect to the position of the virtual atoms linking the QM and the MM regions. The force acting on the atom at the regional boundary is obtained in a simple form based on the total energy conservation. The accuracy of LMM is demonstrated in detail using a system of silicon partitioned into the QM and the MM region at the (100) boundary plane. This condition has been difficult to simulate by conventional methods employing the link atoms because of the strong repulsion between the nearby link atoms.

Keywords: Hybrid quantum mechanical/molecular mechanical simulations; Silicon

1. Introduction

Molecular dynamics (MD) simulations of large-scale systems have been one of the challenging issues in materials science. Quantum mechanical (QM) calculations at the first-principles (FP) level are crucial to providing an accurate description of the system. However, expensive QM calculations often make long-time simulations practically infeasible. Though molecular mechanical (MM) calculations enable long-time simulations,

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they have an inherent transferability problem, resulting in a narrow range of application. It should be noted, however, that in many cases of interest to us, the large-scale system is regarded as consisting of a chemically active region of relatively small size and a large environmental region that is practically inert. Therefore, in order to reduce the computational cost but to retain the accuracy, it is expedient to assign different levels of description to each region: QM calculations for the chemically active region and MM calculations for the environmental region. Based on this idea, the QM/MM hybrid methods have been developed and improved with remarkable applications [1–11].

In the QM/MM hybrid simulations, there are many cases where the regional boundary is required to bisect the covalent bonds between the QM and the MM region. The "link atom approach" is a popular solution to this, in which a virtual atom is used to saturate the broken bond of the QM atom at the boundary. Though this is the most simple and straightforward approach, how to remove the additional degrees of freedom with respect to the position of the link atom is a delicate issue. There have been proposed more sophisticated approaches to describe the coupling between the QM and the MM region at the covalent bonds, e.g., pseudobond scheme [7,8], quantum capping potential scheme [9,10], and effective group potential scheme [11]. These are free of additional atoms and closely related to effective core potential technique. There have been efforts to refine the link atom approach itself. The scaled position link atom method (SPLAM) [1] has provided a successful solution to remove the additional degrees of freedom, which has been the main drawback of the conventional approach. A link atom (a hydrogen atom) is positioned along the direction of the original bond at a distance determined by a simple scaling procedure. The extension of the substitute bond is adjusted to that of the original bond so that the mechanical properties of the original bond are restored. SPLAM was originally devised for the QM/MM hybrid simulation of biological molecules in complex solvents. It gives a good description for simple σ bonds such as the ones between CH_2 groups frequently occurring in proteins. Using this point of view, the method is also applicable to covalent crystals such as silicon.

For silicon, QM/MM hybrid simulations are also expected to be a powerful tool to clarify the formation process of surface nanostructures and reaction process at the surfaces. The surface region, in which significant rearrangement of atoms is expected, needs to be described by QM calculations. A large MM region extending deep into the bulk below the surface region plays an important role in absorbing heat and strain produced in the surface region. A simple way of partitioning the system into the QM and the MM regions is to assume the regional boundary to be parallel to a crystal plane such as (1 1 1) or (1 1 0) of the diamond lattice. These boundary planes bisect one bond per boundary atom, which enables a straightforward application of SPLAM to the QM/MM hybrid system of silicon. From a practical point of view, however, there is another vital choice of the boundary plane, i.e., (1 0 0) plane. In the hybrid simulations focusing on the phenomena related to (1 0 0) surfaces, region partitioning using the (1 0 0) plane is a natural and reasonable choice. It should be noted, however, that in this case, the boundary plane bisects two covalent bonds per boundary atom. Each broken bond needs to be terminated by the link atom. Here, we face a serious problem: the distance between the link atoms is so short that the atoms near the boundary undergo spurious stress due to the strong repulsion between the nearby link atoms. The spurious stress itself would be removed by trying a different type of element, other than hydrogen, for the link atom. However, the scaling procedure would be much more complicated compared to the one used in the original SPLAM. Therefore, a new hybrid method substantially different from SPLAM is highly desirable to describe the bond bisected by the (1 0 0) boundary plane.

In this study, we present a new hybrid method that is free from the spurious stress at the boundary due to the repulsion between the nearby link atoms, and the scaling procedure itself. For this purpose, a link molecule was developed and used instead of a link atom. We call the new method "link molecule method (LMM)." The formalism of the force acting on the boundary atom is derived based on the total energy conservation. The accuracy of the method is demonstrated in detail by making comparison with results of the full QM calculations for the original system.

2. Method

We describe the basics of LMM, drawing a comparison with SPLAM. Fig. 1a shows the atomic structure of bulk silicon, where the QM/MM boundary plane parallel to (1 0 0) is shown by the dotted line. The

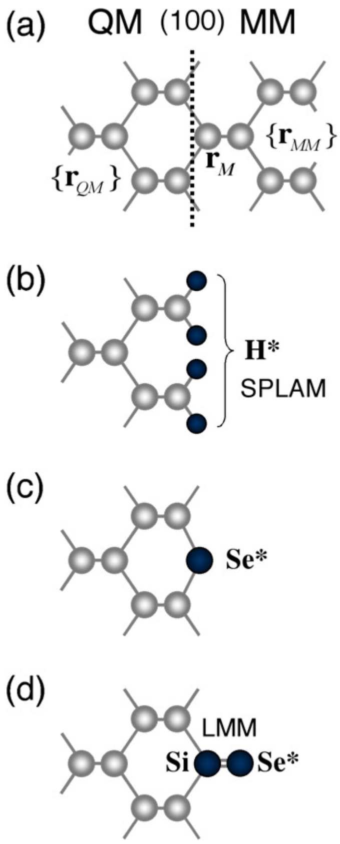

Fig. 1. Schematic illustration of the region partitioning with (1 0 0) boundary plane. (a) Original system. The QM region terminated by (b) pseudo-hydrogen atom, H^*, (c) pseudo-selenium atom, Se^*, and (d) Si–Se^* molecule.

atomic configuration of the QM and that of the MM regions are represented as $\{\mathbf{r}_{QM}\}$ and $(\{\mathbf{r}_{MM}\}, \mathbf{r}_M)$, respectively. Here, $\mathbf{r}_M$ in the latter represents the position of the MM atom bonding to its two neighboring QM atoms at the boundary. It should be noted that the boundary bisects two covalent bonds per boundary atom. If we try to apply SPLAM to this case, a pseudo-hydrogen atom H^* is used to saturate each broken bond of the QM atom at the boundary as shown in Fig. 1b. As mentioned earlier, however, the boundary undergoes spurious stress due to the strong repulsion between the nearby link atoms. At first sight, this problem seems simply a matter of inappropriate choice of the type of link atom for SPLAM. Therefore, it is worth trying to replace each pair of the nearest H^* atoms by another type of a single atom that can fully take on the role of saturating the two broken bonds. For such a new link atom, it is natural to select one from the group VI elements in the periodic table because these elements have two chemical bonds and can saturate the two broken bonds as shown in Fig. 1c. It is crucial to suppress lattice distortion in the FP region due to the difference of electron negativity between Si and the link atom. In this point of view, we focus on selenium, from among the group VI elements. The binding energy of the Se 4p level (−6.5 eV) is closer to that of the Si s-p hybridized orbital (−5 to −6 eV) than any of the other group VI elements. This is a necessary condition to suppress undesirable lattice distortion in the FP region. It is, however, not an adequate condition. Based on the calculated 4p pseudo-potential of Se, the depth and the width of the non-local part are adjusted so as to achieve as much as possible a seamless connection at the QM/MM boundary. The artificial element, referred to as pseudo-selenium (Se^*), is obtained as follows. The core potential is defined for the angular-momentum component l,

$$V_l(r) = \begin{cases} \sum_{k=0}^{6} c_k r^{2k}, & r < r_{cl} \\ V(r), & r \geqslant r_{cl} \end{cases} \tag{1}$$

where r_{cl} are chosen cutoff radius for l, and $V(r) = -Z_v/r$ with Z_v the number of valence electron ($Z_v = 6$). The seven coefficients $\{c_k\}$ are determined from the seven conditions, $V_l(0) = V_{cl}$, $V_l'(0) = 0$, and $V_l^{(n)}(r_{cl}) = V^{(n)}(r_{cl})$ ($n = 0, 1, 2, 3, 4$). For a given set of the values of r_{cl} and V_{cl}, this potential is used in the self-consistent-field calculations to determine the electron density and the energy level. This procedure is continued until the set of the values which yields the desirable value of the energy level is found. Finally, the Troullier–Martins type [12] pseudopotentials are constructed using the same values of r_{cl}. The following set are used to generate the Se* pseudopotentials: $(r_{cs}, r_{cp}, r_{cd}) = (1.8, 1.9, 2.0)$ [a.u.] and $(V_{cs}, V_{cp}, V_{cd}) = (-1.389, -3.433, -8.560)$ [hartree]. The unscreened semi-local pseudopotentials are shown for Se* in Fig. 2(right), together with those for Se (left). Though the distortions of the bond length and angle in the FP region are reduced by using Se* as the new link atom, they are not completely negligible. It should also be noted that the scaling procedure for the Se* position inevitably becomes much more complicated than the original SPLAM, because the Se* shakes hands with the two Si atoms whose degrees of freedom are independent of each other. Moreover, the total energy is not conserved in the current formulation. Therefore, rather than pursuing an extension of SPLAM, we need to take an approach substantially different from SPLAM.

After several attempts, we came upon the idea of introducing an additional Si atom to terminate the FP region along with the Se* atom [13,14] as shown in Fig. 1d. The additional Si atom is crucial not only in reducing the harmful effect of the Se* atom on the FP region to a negligible value, but also in developing a scaling free coupling scheme. The positions of the Si and the Se* atoms of the virtual molecule, referred to as the link molecule, are represented as $\mathbf{r}_{L(Si)}$ and $\mathbf{r}_{L(Se^*)}$, respectively. As will be shown later, the atomic configuration $(\{\mathbf{r}_{QM}\}, \mathbf{r}_{L(Si)})$ obtained from a full optimization of the QM region terminated by the link molecule is nearly the same as the atomic configuration $(\{\mathbf{r}_{QM}\}, \mathbf{r}_M)$ obtained from a full optimization by QM calculations of the original system. This provided a major incentive to develop a scaling free coupling scheme using the link molecule. We assume that the length of the link molecule is fixed at the equilibrium value and that the molecular axis is always oriented [1 0 0]. Consequently, the additional degrees of freedom are left only for $\mathbf{r}_{L(Si)}$, which are removed by putting the Si atom of the link molecule at the position of the boundary Si atom of the MM region ($\mathbf{r}_M$ in Fig. 1a) at every MD step. Our approach is thus scaling free and substantially different from SPLAM. We call the present method "Link Molecule Method (LMM)."

The force on each atom of the hybrid system is derived as follows. The total energy is represented as $E = U + T$, where

$$U = U_{QM}(\{\mathbf{r}_{QM}\}, \mathbf{r}_{L(Si)}, \mathbf{r}_{L(Se^*)}) + U_{MM}(\{\mathbf{r}_{MM}\}, \mathbf{r}_M), \tag{2}$$

$$T = T_{QM}(\{d\mathbf{r}_{QM}/dt\}) + T_{MM}(\{d\mathbf{r}_{MM}/dt\}, d\mathbf{r}_M/dt). \tag{3}$$

In Eq. (2), U_{QM} and U_{MM} represent the potential energy of the QM region and the MM region, respectively. Similarly, in Eq. (3), T_{QM} and T_{MM} represent the atomic kinetic energy of the corresponding regions, respectively. It should be noted that the contribution from the link molecule is excluded from Eq. (3). Requiring the total energy conservation, we obtain the force on the atom at $\mathbf{r}_M$,

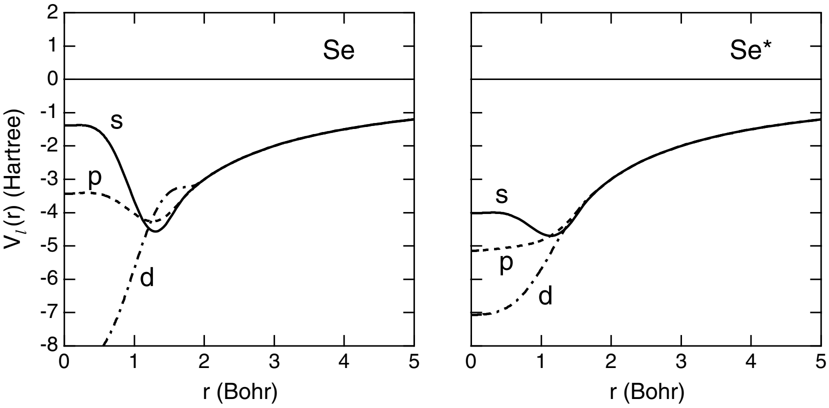

Fig. 2. Ion-core pseudo-potentials ($l = 0, 1, 2$) for selenium (left) and pseudo-selenium (right).

$$\mathbf{f}_{\mathrm{M}} = -\frac{\partial U_{\mathrm{MM}}}{\partial \mathbf{r}_{\mathrm{M}}} + \mathbf{f}_{\mathrm{L(Si)}} + \mathbf{f}_{\mathrm{L(Se^*)}}. \tag{4}$$

Here, $\mathbf{f}_{\mathrm{L(Si)}}$ and $\mathbf{f}_{\mathrm{L(Se^*)}}$ are the force on the Si atom and that of the Se* atom of the link molecule, respectively,

$$\mathbf{f}_{\mathrm{L(Si)}} = -\frac{\partial U_{\mathrm{QM}}}{\partial \mathbf{r}_{\mathrm{L(Si)}}}, \quad \mathbf{f}_{\mathrm{L(Se^*)}} = -\frac{\partial U_{\mathrm{QM}}}{\partial \mathbf{r}_{\mathrm{L(Se^*)}}}. \tag{5}$$

The sum of the force acting on the link molecule is interpreted as a part of the force acting on the boundary MM atom, $\mathbf{f}_{\mathrm{M}}$.

3. Results and discussions

The present hybrid method, LMM, was tested in detail using a slab system of silicon consisting of 28 layers with Si (100) 1 × 1 surface periodicity (Fig. 3a). The original system was partitioned into the QM and the MM regions by the (100) plane between the 11th and the 12th layers. The QM region was terminated by the link molecule as shown in Fig. 3b. We used the hybrid simulation package CAMUS-FSIS [15]. A standard FP calculation code based on the density functional theory with pseudo-potentials and plane wave basis set, PHASE [15], is incorporated into the hybrid simulation package for the calculations of the QM subsystem. In the present study, the wave functions are expanded in a plane wave basis set with a 9 Ry cutoff inside a tetragonal quantum box of 51.117 × 7.229 × 7.229 [a.u.^{3}], and 8 special k points in the irreducible Brillouin zone were used. The energy criterion for wave function convergence is 10^{-10} hartree. LDA-PW91 [16] is used for the exchange and correlation part of the Kohn–Sham Hamiltonian. The MM calculations were performed using a Stillinger–Weber type potential [17]. The value of the parameters of the original paper were modified in the present study to reproduce bulk properties obtained from the QM calculations [18].

First, we compared the equilibrium structure of the QM region terminated by the link molecule with that of the corresponding region of the original system calculated by the full QM calculations. The force on each atom is less than 10^{-4} [a.u.] in the equilibrium structures. Table 1 shows the resultant distances between the neighboring atoms. The results of the QM region terminated by the link molecule (third row in Table 1) show good agreement with those obtained from the full QM calculations of the original system (second row in Table 1). The link molecule thus successfully works in reproducing the equilibrium atomic structure of the QM region with high accuracy.

Next, we examined the hybrid system under deformation to see how accurately mechanical properties of the bond at the QM/MM boundary are restored. With the atomic configuration of the MM region kept rigid in its equilibrium configuration, the position of the MM region was displaced by a small amount relative to the QM region in the three orthogonal directions represented by the x, y, and z directions in the right bottom in Fig. 3. The results are shown in Fig. 4, in which the horizontal axis represents the amount of displacement of the MM region, and the vertical axis represents the components of the force. The solid circles, triangles, and diamonds represent the results for the atoms labeled 10, 11, and 12 of the hybrid sys-

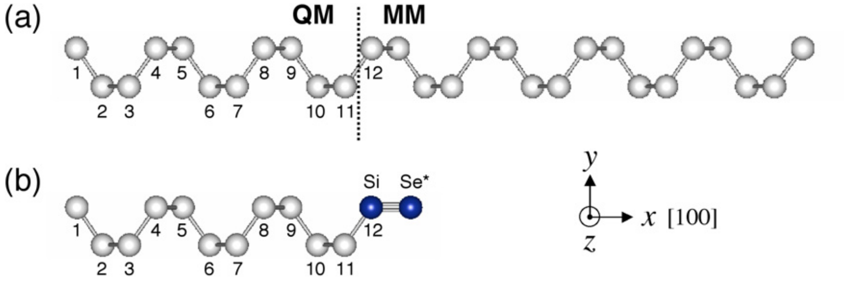

Fig. 3. (a) The region partitioning of the system used for accuracy checks on the link molecular method. (b) The QM region terminated by the link molecule, Si–Se*.

Table 1
The equilibrium distances $r_{i,j}$ [Å] between the atoms labeled i and $i+1$ in Fig. 3

	$r_{1,2}$	$r_{2,3}$	$r_{3,4}$	$r_{4,5}$	$r_{5,6}$	$r_{6,7}$	$r_{7,8}$	$r_{8,9}$	$r_{9,10}$	$r_{10,11}$	$r_{11,12}$
(a)	2.312	2.340	2.347	2.352	2.349	2.349	2.347	2.346	2.346	2.346	2.346
(b)	2.314	2.340	2.347	2.352	2.349	2.351	2.347	2.347	2.345	2.354	2.338
|(a)–(b)|	0.002	0.000	0.000	0.000	0.000	0.002	0.000	0.001	0.001	0.008	0.008

The second and the third rows represent results of the original system (Fig. 3a) obtained from full QM calculations and those of the QM region terminated by Si–Se* (Fig. 3b), respectively. The length of the link molecule (Si–Se*) is 2.002 Å in the equilibrium structure.

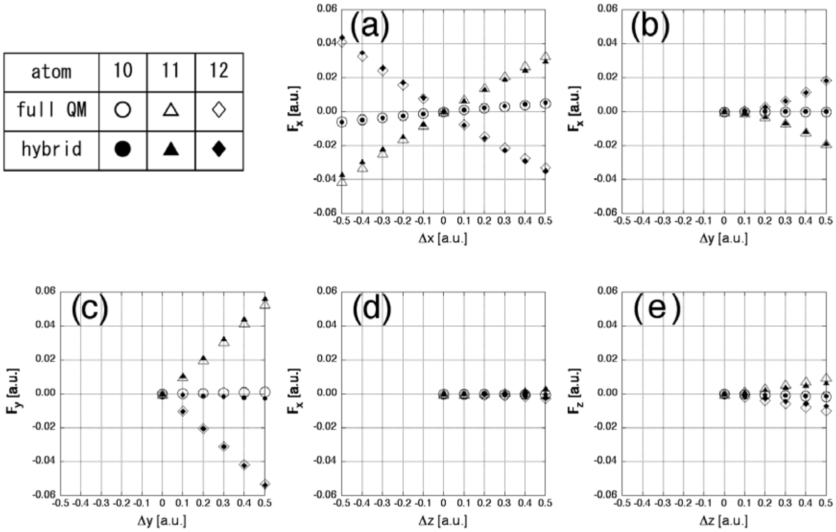

Fig. 4. Results of the force acting on the atoms labeled 10, 11, and 12 of the system in Fig. 3a under deformation. "Full QM" denotes the full QM calculations of the original system, and "hybrid" the hybrid calculations with LMM.

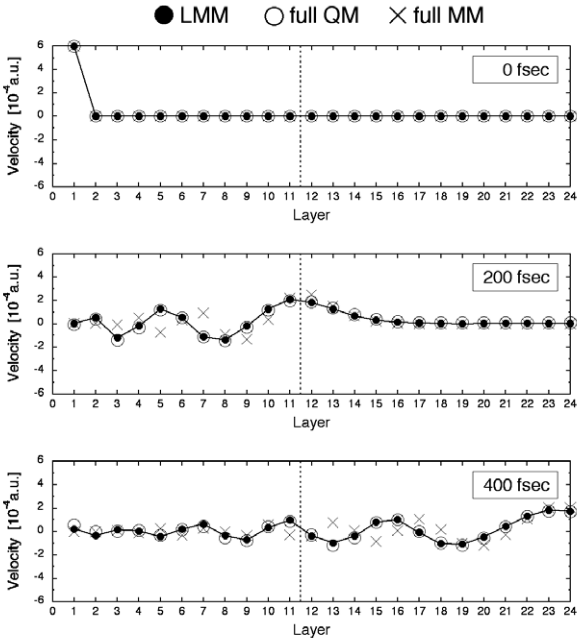

Fig. 5. Results of velocity propagation simulations for the system in Fig. 3a. Velocity distributions obtained from the hybrid, the full QM and the full MM calculations are shown.

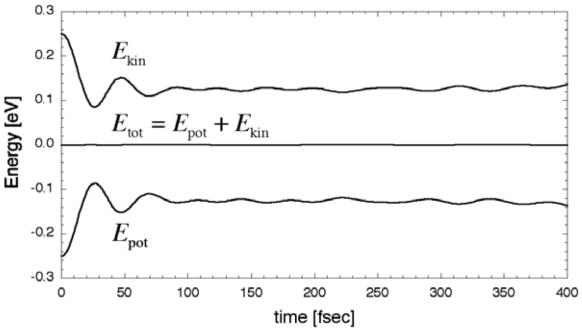

Fig. 6. The kinetic energy (E_{kin}), the potential energy (E_{pot}), and the total energy (E_{tot}) obtained from the velocity propagation simulation of the QM/MM hybrid system in Fig. 3a.

tem, respectively. The corresponding results obtained from the full QM calculations of the original system are also shown for comparison by open circles, triangles, and diamonds, respectively in Fig. 4. The results of the full QM calculations are reproduced with high accuracy by LMM, which also successfully covers anharmonicities as we see in Fig. 4b.

Finally, we examined the trajectory of the dynamics of the system by performing velocity propagation simulations. The initial velocity ($V_0 = 6$ [a.u.]) toward [100] is applied to the left edge atom of the system in Fig. 3a, and the evolution of the velocity distribution is monitored. The results of the hybrid calculations are shown by closed circles in Fig. 5, in which the calculations of the full QM (open circles) and the full MM (crosses) of the original system are also shown for comparison. The position of the QM/MM boundary is drawn by the vertical broken line as a guide for the eye. The results of the hybrid calculations show good agreement with those of the full QM calculations, giving a much more reliable description compared to the full MM calculations. The total energy of the hybrid system is conserved with high accuracy during the simulation as shown in Fig. 6. A reliable description of the seamless coupling of the QM and the MM regions at the (100) boundary is thus successfully achieved by LMM.

4. Conclusions

In conclusion, we have presented a new hybrid method to couple the QM and the MM regions at the Si (100) boundary plane. A link molecule consisting of a silicon and a pseudo-selenium atom has been developed and used to terminate the broken bonds of the QM atoms at the boundary. We call the method “link molecule method (LMM).” LMM is free from the problem of the spurious stress at the boundary due to the repulsion between the link atoms, which the existing hybrid method inevitably encounters. Moreover, LMM is free from the scaling procedure. The formalism of the force acting on the boundary atom was derived based on total energy conservation. The accuracy of the method has been demonstrated in detail by making comparison with results of the full QM calculations for the original systems. In the present study, the FP calculations have been used to describe the QM region, and the pseudo-selenium atom is incorporated into the link molecule. The resultant link molecule is guaranteed to work for the QM/MM hybrid simulations with Si (100) boundary plane. The basics of the scaling free hybrid scheme using a link molecule are also able to be extended to the case where the QM region is described by tight-binding (TB) calculations. In this case, an appropriate link molecule to terminate the TB region, which is not necessarily a Si–Se* molecule, will be able to be constructed by adjusting TB parameters for the link molecule.

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$$f_2(r) = \begin{cases} A(Br^{-p} - r^{-q})\exp[(r-a)^{-1}], & r < a \\ 0, & r \geqslant a. \end{cases} \tag{6}$$

The reduced three-body potential has the following form:

$$f_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}), \tag{7}$$

where θ_{jik} represents the angle between $\mathbf{r}_j$ and $\mathbf{r}_k$ subtended at vertex i, and

$$\begin{aligned} &h(r_{ij}, r_{ik}, \theta_{jik}) \\ &= \begin{cases} \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] \\ \times(\cos\theta_{jik} + 1/3)^2, \quad r_{ij} < a \text{ and } r_{ik} < a \\ 0, \quad r_{ij} \geqslant a \text{ or } r_{ik} \geqslant a. \end{cases} \end{aligned} \tag{8}$$

In the present study, the value of the parameters of the original paper were modified to reproduce bulk properties obtained from the QM calculations as follows:

$$\begin{aligned}
&A = 7.023021541, \quad B = 0.5971098806, \\
&p = 4.030516642, \quad q = 0.03962373947, \quad a = 1.8, \\
&\lambda = 21.0, \quad \gamma = 1.2, \\
&\sigma = 0.20954\ \text{nm}, \quad \varepsilon = 2.16026\ \text{eV}.
\end{aligned} \tag{9}$$

In addition, a constant energy shift, -37.594934 eV/atom, is added to the total energy of the MM system.