

## Multibody expansion of particle interactions: How many-body is a particular element in a cluster

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The particle-particle interaction potential of an  $N$ -atom cluster is expanded in  $n$ -body contributions. The expansion allows us to determine the magnitude of each one of the  $n$ -body terms, and consequently quantifies how  $n$ -body a potential really is. This way we obtain bounds for the relative error due to truncation, a feature that could be applicable in several contexts like the search of minimal energy cluster conformations, to obtain adequate seeds for further *ab initio* refinement, or to speed up molecular dynamics computations. We develop the formalism, and test the procedure numerically for the Lennard-Jones, Murrell-Mottram, Gupta, and Sutton-Chen potentials. The contributions of the  $n$ -body terms for Ag, Al, Au, Co, Cu, Fe, Ir, Ni, Pb, Pd, Pt, and Rh clusters are computed up to  $n = 9$ ; they show that the importance and magnitude of the  $n > 2$  interaction terms depend on the particular element. The relevance of the  $n$ -body corrections as a function of cluster size is also explored for  $N \leq 50$ , and for a linear chain of  $N \leq 1000$  atoms.

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### I. INTRODUCTION

Nanoclusters have attracted the interest of physicists, chemists, and applied scientists, due to their challenges to basic science and because of the variety of potential and actual technological uses they have [1]. From a basic science point of view they constitute a natural bridge between the macroscopic bulk limit and the microscopic scale of atoms and molecules. On the application side they have found a large variety of uses in technologies that span the range from catalytic processes, to hydrogen conversion, to increasing the octane grade of gasolines, all the way to optoelectronics.

But, as Goedecker *et al.* [2] recently pointed out, the first and most fundamental step in the description and understanding of clusters is the precise determination of the geometrical configuration that the constituent atoms do adopt, since most physical properties depend on the structure of the system. This fact has generated significant interest and activity in the field.

However, the complexity of the problem is quite overwhelming as can easily be perceived by pointing out that a 13-atom cluster, interacting via a simple Lennard-Jones two-body potential, has a potential energy surface function with around 1000 minima [3]. Even more impressive is that for a 147-atom cluster this number grows to  $\sim 10^{50}$  minima [4]. However, it is generally accepted that two-body potentials, such as the Lennard-Jones potential, do not yield an accurate description of the complex interatomic interactions in a cluster. Consequently, *ab initio* approaches to handle these interactions have become the standard in the literature, especially when the number of atoms is not too large. However, the ideal procedure of implementing an unbiased search using exclusively *ab initio*, or density functional theory (DFT) codes, is at present out of the question for large clusters, because of

the extremely long number crunching times that are required. Thus, a number of strategies [5–10] have been put forward to approach this problem, such as (i) using two-body [4,6,11,12] or more refined phenomenological potentials [13–15] and global optimization techniques to obtain, rather quickly, putative minimum energy configurations; (ii) using less expensive quantum methods, like tight binding, to compute structural [16] and even magnetic properties [17–20] of larger clusters ( $N > 100$ ); or (iii) using a phenomenological potential to construct a bank of diverse structures that are subsequently refined by *ab initio* approaches [21–25]. Using the latter approaches it becomes apparent that the minimum energy cluster structure obtained with phenomenological potentials does not necessarily converge to the one with the lowest energy after DFT refinement [25]. Hence, a robust approach should rely on constructing a diverse enough set of structures that could be obtained, for example, as minimal structures of a potential that has some similarities to the exact one (i.e., obtained from an *ab initio* calculation) but that are simple enough to compute.

In this context a number of many-body phenomenological potentials have been developed, in the hope that a reasonable approximation to the interatomic interactions can be found. For example, Murrell and Mottram [26] truncated the interaction beyond three-body terms. Other potentials, like the one by Gupta [15,27], are intrinsically of many-body type and do not have an explicit expansion as  $n$ -body potentials. However, there is no consistent method to determine how relevant each one of these expansions is, except for a fitting of the error. For example, there is no physical picture to decide if it makes sense to construct a full multibody potential, such as the one by Gupta [27], or if it is enough to truncate by means of a particular  $n$ -body description, such as Murrell and Mottram did. A similar argument can be made when choosing among different many-body potentials, such as Gupta or Sutton-Chen [28].

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Here we offer a method to decompose the potential that describes the atomic interactions in a cluster, in terms of an  $n$ -body potential expansion, that applies both to phenomenological potentials, and potentials obtained from *ab initio* approaches. It is interesting to notice that such an expansion into  $n$ -body terms could also provide physical information and intuitive understanding about the relevant mechanisms that determine the cluster structure. Furthermore, such an expansion can be used to assert “how many body” the interaction of the atoms that form the cluster really is, within a given tolerance. This certainly may be combined with a search strategy of the type mentioned above, to construct a bank of diverse conformations that are subsequently refined by *ab initio* approaches.

This paper is organized as follows: after this Introduction, in Sec. II we present the basic ideas about the  $n$ -body expansion. In Sec. III we apply the method to a number of elements, to determine how relevant each one of the  $n$ -body terms is. Finally, Sec. IV closes the paper with an analysis of the method and a discussion of the results that are obtained.

## II. EXPANSION INTO $n$ -BODY INTERACTION TERMS

We start by assuming that the interactions between  $N$  identical particles can be expanded using a Born-Oppenheimer type approximation, namely

$$U_{\text{total}} = \sum_{n=2}^N U_n, \quad (1)$$

where  $N$  is the number of particles in the system, and  $U_n$  represents  $n$ -body interaction terms. The total potential energy  $U_{\text{total}} = U[R_N(\vec{i}_N^N)]$  depends in general on the position  $\vec{r} \rightarrow (x, y, z)$  of all  $N$  particles, where  $R_N(\vec{i}_N^N)$  is the set of all possible  $N(N-1)/2$  different pairwise distances  $r_{ij} = |\vec{r}_i - \vec{r}_j|$  that can be formed with the  $N$  particles labeled by  $\vec{i}_N^N = (1, 2, 3, \dots, N)$ . It is important to remember that the particles are indistinguishable. Similarly, let us consider an  $n$ -body potential  $u_n[R_n(\vec{i}_n^N)]$  that depends on  $n(n-1)/2$  variables, which correspond to all the different pair distances that can be formed with the position of the  $n$  particles labeled by  $\vec{i}_n^N = (i_1, i_2, \dots, i_n)$ , for  $1 \leq k \leq n \leq N$ . Since the  $n$  particles are chosen from the larger set of  $N$  particles. Hence, for an  $n$ -body potential that describes an  $N$ -particle cluster, the set  $\Xi_n^N$  is composed of all the  $N!/n!(N-n)!$  different subsets of  $n$  particles labeled by  $\vec{i}_n^N = (i_1, i_2, \dots, i_n)$ . They are chosen from the set of  $N$  particles, so that

$$U_n = \sum_{\vec{i}_n^N \in \Xi_n^N} u_n[R_n(\vec{i}_n^N)]. \quad (2)$$

For example, in the case of a two-body potential we can write  $\vec{i}_2^N = (i, j)$  with  $R_2(i, j) = \{r_{ij}\}$ , so that the two-body contribution can be written as

$$U_2 = \sum_{\vec{i}_2^N \in \Xi_2^N} u_2[R_2(\vec{i}_2^N)] = \sum_{i=1}^N \sum_{j>i}^N u_2(r_{ij}). \quad (3)$$

For a three-body potential we use  $\vec{i}_3^N = (i, j, k)$  with  $R_3(i, j, k) = \{r_{ij}, r_{ik}, r_{jk}\}$ , from which we obtain

$$U_3 = \sum_{\vec{i}_3^N \in \Xi_3^N} u_3[R_3(\vec{i}_3^N)] = \sum_{i=1}^N \sum_{j>i}^N \sum_{k>j}^N u_3(r_{ij}, r_{ik}, r_{jk}). \quad (4)$$

Iterating this procedure the potential  $U$  can be expanded in a basis of  $n$ -body potentials  $\{u_n\}$ , as

$$U[R_N(\vec{i}_N^N)] = \sum_{n=2}^N \sum_{\vec{i}_n^N \in \Xi_n^N} u_n[R_n(\vec{i}_n^N)] = \sum_{n=2}^N U_n. \quad (5)$$

Notice that if we change the particle order we still obtain the same result, which is consistent with particle indistinguishability.

Up to this point all is completely general, but we are interested in a well defined basis  $\{u_1, u_2, \dots, u_N\}$ . In other words, a basis where  $u_n$  only represents the  $n$ -body interactions, so that  $u_n$  must vanish when two or more particles are infinitely far apart. From this observation and Eq. (5) we conclude that if we expand  $U$  in a well defined basis, then in the limit where  $m$  particles are far apart from particle  $n$ , the expansion has to converge to an  $(N-m)$ -body expansion, namely

$$U[R_N(\vec{i}_N^N)] \rightarrow \sum_{n=2}^{N-m} \sum_{\vec{i}_n^N \in \Xi_n^{N-m}} u_n[R_n(\vec{i}_n^{N-m})]. \quad (6)$$

Therefore, we should define the two-body potential  $u_2$  by the limit when all but two particles are infinitely far apart

$$U[R_N(\vec{i}_N^N)] \rightarrow U_2(r) = u_2(r). \quad (7)$$

It can be proven that when we choose  $u_2$  by means of Eq. (7) we are also choosing this well defined basis. From Eq. (5) it follows that we can define the following recurrence relation:

$$\begin{aligned} u_n[R_n(\vec{i}_n^N)] &= \sum_{\vec{i}_n^N \in \Xi_n^N} u_n[R_n(\vec{i}_n^N)] \\ &= U[R_n(\vec{i}_n^N)] - \sum_{k=2}^{n-1} \sum_{\vec{i}_k^N \in \Xi_k^N} u_k[R_k(\vec{i}_k^N)]. \end{aligned} \quad (8)$$

Notice that here  $U[R_n(\vec{i}_n^N)]$  is the total potential energy of  $n$  particles. Equations (7) and (8) provide a recursive definition for the construction of the well defined basis sets of  $n$ -body potentials  $\{u_n\}$  that properly represents the  $n$ -body interactions. Hence, through this approach the  $n$ -body potentials can be computed iteratively from the potentials generated for  $k = 2, 3, 4, \dots, n-1$ . For example, consider a potential  $U$  describing the interaction of  $N = 3$  particles. According Eq. (7) the well defined two-body potential is given by

$$u_2(r_{12}) = \lim_{r_{13}, r_{23} \rightarrow \infty} U(r_{12}, r_{13}, r_{23}), \quad (9)$$

when the third particle is far away. Hence, Eq. (8) implies that the well defined three-body potential is given by

$$u_3(r_{12}, r_{13}, r_{23}) = U(r_{12}, r_{13}, r_{23}) - \sum_{i=1}^3 \sum_{j>i}^3 u_2(r_{ij}). \quad (10)$$

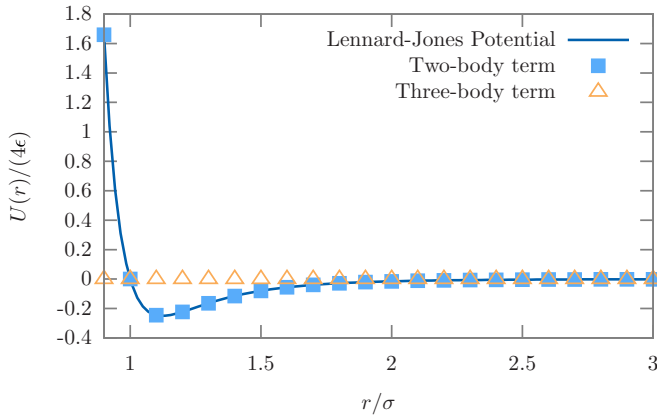


FIG. 1. Comparison between the Lennard-Jones potential and the expansion obtained with our algorithm. Only the two-body term is nonzero.

Notice that if we replace  $u_2$  and  $u_3$  in Eq. (5) we obtain  $U$ , and in the limit  $r_{13}, r_{23} \rightarrow \infty$  we have that  $u_3 \rightarrow 0$ , as expected. Hence, the  $n$ -body potential is calculated recursively from clusters of sizes smaller than  $n$ . Combining Eqs. (7) and (8) we find an explicit form to compute the  $n$ -body potentials, given by

$$u_n[R_n(\vec{r}_n)] = \sum_{k=2}^n (-1)^{k-n} \sum_{\vec{r}_k \in \Xi_k^n} U[R_k(\vec{r}_k)]. \quad (11)$$

In Fig. 1 we show the two- and three-body expansion of a Lennard-Jones potential, which shows that, as expected, the three-body contribution vanishes. The calculation is done iteratively from  $N = 2$  and  $N = 3$  clusters. Similarly, we take a Murrell-Mottram potential [26], which has two- and three-body terms, and plot the respective contributions, shown in Fig. 2. Assuming that all pairwise distances are the same, namely  $r = r_{ij}$ , the two-, three-, and four-body terms are displayed as  $u_2(r)$ ,  $u_3(r, r, r)$ , and  $u_4(r, r, r, r, r, r)$ , respectively, and they are calculated from  $N = 2$ ,  $N = 3$ , and  $N = 4$

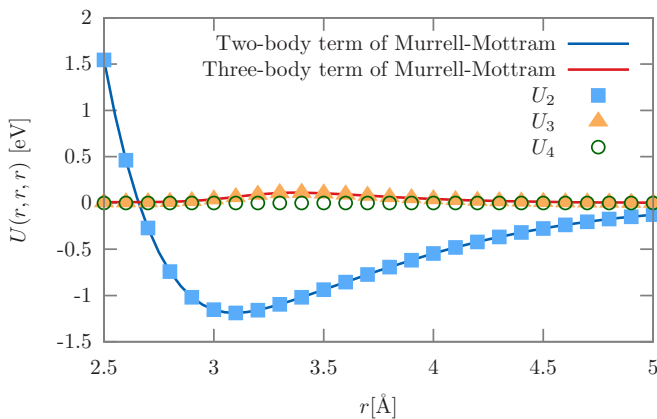


FIG. 2. Comparison between the two- and three-body expansion terms for the Murrell-Mottram potential as obtained with our algorithm. For the case of the three-body expansion we plot  $u_3(r, r, r)$ . For the four-body expansion we plot  $u_4(r, r, r, r, r, r)$ . The parameters we use are for Li.

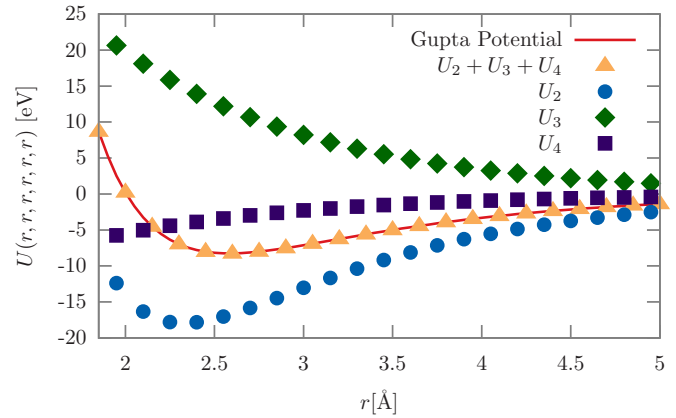


FIG. 3. Two-, three-, and four-body expansion terms of the Gupta potential obtained with our algorithm for  $N = 4$ , and the comparison between the sum of the terms and the full Gupta potential. We use Al parameters.

clusters. The higher order  $n$ -body potentials ( $n > 3$ ) are zero, independent of  $N$ , verifying that our basis generates the expected expansion.

The same strategy can be applied to potentials that are inherently many-body, such as the widely used Gupta [27] or Sutton-Chen [28] potentials. In Figs. 3 and 4 we display the  $n$ -body expansion of the Gupta and Sutton-Chen potentials, respectively, calculated from  $N = 2$  through  $N = 4$  clusters. Using the same notation as in Fig. 2 we compare the Gupta potential (evaluated at  $r_{ij} = r$  for all  $i$  and  $j$ ) so that the expansion yields

$$U(r) = 6u_2(r) + 4u_3(r, r, r) + u_4(r, r, r, r, r, r), \quad (12)$$

and in this case the higher order contributions become nonzero contrary to the Murrell-Mottram potential results of Fig. 2.

It is apparent that the relative contributions of the  $n$ -body terms depend on the many-body potential that is used. Hence we can employ the relative magnitude of each term in the  $n$ -body expansion to compare different many-body potentials. This allows us to select a particular many-body potential

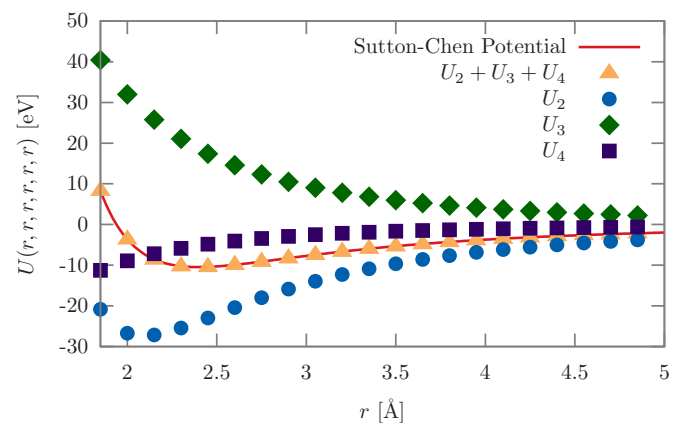


FIG. 4. Two-, three-, and four-body expansion terms of the Sutton-Chen potential obtained with our algorithm for  $N = 4$ , and the comparison between the sum of the terms and the full Sutton-Chen potential. We use Al parameters.

that has the largest contribution for the lowest  $n$ -body terms. This is useful when comparing and approximating the atomic interactions in a clusters, obtained by *ab initio* methods, in terms of a simple  $n$ -body expansion; for example, when using the strategy outlined above.

### III. ESTIMATING THE RELEVANCE OF THE $n$ -BODY TERMS FOR A GIVEN ELEMENT

We can estimate how relevant the  $n$ -body contribution to the  $N$ -body expansion of a given cluster of size  $N$  is by averaging the absolute value of the  $n$ -body term

$$U_n = \sum_{\vec{i}_n \in \Xi_N} u_n[R_n(\vec{i}_n)], \quad (13)$$

over the available phase space; namely, over a large set  $C_N$  of suitable (see below) randomly generated clusters of size  $N$ . Hence, we can define this contribution as

$$P_n = \frac{1}{P_T} \sum_{A \in C_N} |U_n(A)|, \quad (14)$$

where the summation is over all clusters  $A \in C_N$ , and the normalization  $P_T = \sum_{n=2}^N \sum_{A \in C_N} |U_n(A)|$ . With this definition we can quantify the contribution of each term over the phase space, so that we can correctly evaluate a tolerable truncation of the potential. Furthermore, we can assert how  $n$ -body the interactions of the atoms in a cluster, as a function of  $N$ , are.

We start by estimating the contribution of each  $n$ -body term from the Gupta potential as a function of the total number of atoms  $N$  in the cluster. We generate a random set of  $3N$  coordinates, in a cubic box of volume  $a^3 N$ , where  $a$  is 4 times the respective dimer equilibrium distance, but we only allow interatomic distances that are larger than a certain value  $r_{\min}$ , since two-body terms diverge as  $r \rightarrow 0$ . To choose this minimal distance we adopt the radius corresponding to the minimal value  $u_{\min}$  of  $u_2$  and we define  $r_{\min}$  as  $u_2(r_{\min}) = -u_{\min}$ . The  $n$ -body contribution average is calculated for  $M$  clusters. In Fig. 5 we display the  $n$ -body contribution as a function of  $N$ . For this particular element (Al), we notice that on average, up to  $N = 9$ , within 50% accuracy the potential is

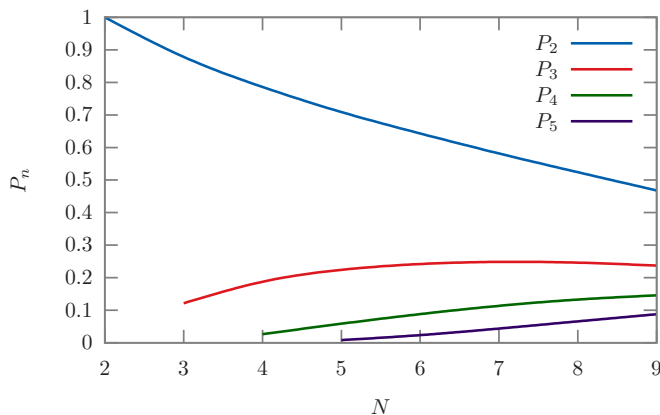


FIG. 5. Contribution of the  $n$ -body expansion terms of the Gupta potential with Al parameters. The data are obtained from  $M = 10^5$  clusters.

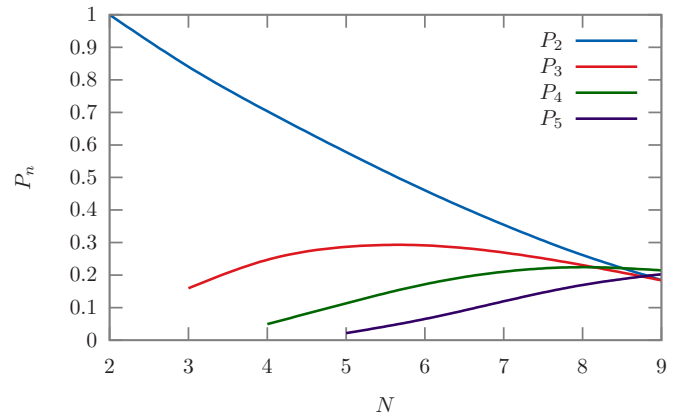


FIG. 6. Contribution of the  $n$ -body expansion terms of the Sutton-Chen potential with Al parameters. The data are obtained from  $M = 10^5$  clusters.

mainly two-body. Hence, in principle if we are willing to risk a 50% error we can perform, for example, molecular dynamics simulations with just the two-body term. Similarly, we could use the two-body term (or any higher  $n \leq N$  order expansion) as a phenomenological potential to search for a large set of minima that can be used as seeds for *ab initio* relaxations applying the above strategy, in an attempt to later find the global *ab initio* minimum.

We implement the same technique to determine the relevance of each of the  $n$ -body terms of the Sutton-Chen Al potential, as shown in Fig. 6. We observe that, in this case, the two-body interaction decays much faster with  $N$  than the Gupta potential, suggesting that for Al a two-body expansion of the Gupta potential may be more appropriate when implementing a molecular dynamics simulation or a minimization strategy.

In Fig. 7 and Table I we compare the relevance of the  $n$ -body expansion of clusters of size  $N = 9$ , using the Gupta potential for different elements. The parameters corresponding to the Gupta potential for Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, Al, and Pb have been extracted from Cleri *et al.* [29], and the parameters

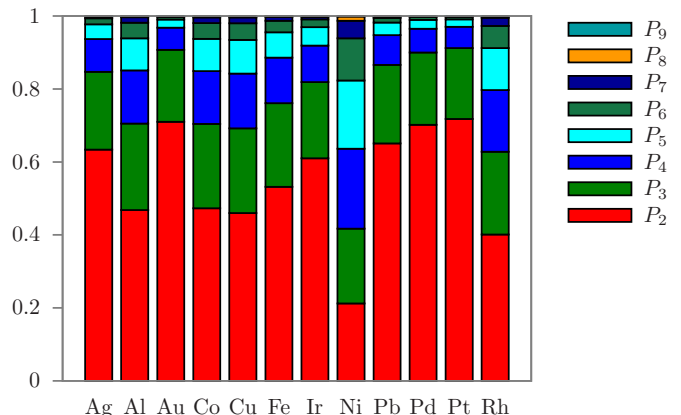


FIG. 7. Contribution of the  $n$ -body expansion terms of the nine-body Gupta potential for different elements. The data is obtained from  $M = 10^5$  different seeds.

TABLE I. Contribution of the  $n$ -body expansion terms of nine-atom cluster using the Gupta potential. The data are obtained from  $M = 10^5$  clusters.

	$P_2$	$P_3$	$P_4$	$P_5$	$P_6$	$P_7$	$P_8$	$P_9$
Ag	$6.34 \times 10^{-1}$	$2.13 \times 10^{-1}$	$8.97 \times 10^{-2}$	$4.07 \times 10^{-2}$	$1.63 \times 10^{-2}$	$4.97 \times 10^{-3}$	$9.74 \times 10^{-4}$	$9.03 \times 10^{-5}$
Al	$4.68 \times 10^{-1}$	$2.37 \times 10^{-1}$	$1.46 \times 10^{-1}$	$8.78 \times 10^{-2}$	$4.28 \times 10^{-2}$	$1.49 \times 10^{-2}$	$3.23 \times 10^{-3}$	$3.23 \times 10^{-4}$
Au	$7.10 \times 10^{-1}$	$1.97 \times 10^{-1}$	$6.11 \times 10^{-2}$	$2.21 \times 10^{-2}$	$7.43 \times 10^{-3}$	$1.97 \times 10^{-3}$	$3.45 \times 10^{-4}$	$2.94 \times 10^{-5}$
Co	$4.73 \times 10^{-1}$	$2.31 \times 10^{-1}$	$1.45 \times 10^{-1}$	$8.84 \times 10^{-2}$	$4.34 \times 10^{-2}$	$1.52 \times 10^{-2}$	$3.30 \times 10^{-3}$	$3.32 \times 10^{-4}$
Cu	$4.60 \times 10^{-1}$	$2.32 \times 10^{-1}$	$1.50 \times 10^{-1}$	$9.24 \times 10^{-2}$	$4.55 \times 10^{-2}$	$1.60 \times 10^{-2}$	$3.47 \times 10^{-3}$	$3.49 \times 10^{-4}$
Fe	$5.32 \times 10^{-1}$	$2.29 \times 10^{-1}$	$1.25 \times 10^{-1}$	$6.93 \times 10^{-2}$	$3.17 \times 10^{-2}$	$1.05 \times 10^{-2}$	$2.20 \times 10^{-3}$	$2.15 \times 10^{-4}$
Ir	$6.10 \times 10^{-1}$	$2.09 \times 10^{-1}$	$1.00 \times 10^{-1}$	$5.03 \times 10^{-2}$	$2.15 \times 10^{-2}$	$6.83 \times 10^{-3}$	$1.38 \times 10^{-3}$	$1.31 \times 10^{-4}$
Ni	$2.12 \times 10^{-1}$	$2.05 \times 10^{-1}$	$2.19 \times 10^{-1}$	$1.87 \times 10^{-1}$	$1.16 \times 10^{-1}$	$4.77 \times 10^{-2}$	$1.17 \times 10^{-2}$	$1.30 \times 10^{-3}$
Pb	$6.51 \times 10^{-1}$	$2.15 \times 10^{-1}$	$8.16 \times 10^{-2}$	$3.42 \times 10^{-2}$	$1.30 \times 10^{-2}$	$3.77 \times 10^{-3}$	$7.17 \times 10^{-4}$	$6.54 \times 10^{-5}$
Pd	$7.02 \times 10^{-1}$	$1.98 \times 10^{-1}$	$6.51 \times 10^{-2}$	$2.42 \times 10^{-2}$	$8.35 \times 10^{-3}$	$2.27 \times 10^{-3}$	$4.08 \times 10^{-4}$	$3.50 \times 10^{-5}$
Pt	$7.18 \times 10^{-1}$	$1.94 \times 10^{-1}$	$5.84 \times 10^{-2}$	$2.05 \times 10^{-2}$	$6.78 \times 10^{-3}$	$1.79 \times 10^{-3}$	$3.14 \times 10^{-4}$	$2.66 \times 10^{-5}$
Rh	$4.01 \times 10^{-1}$	$2.27 \times 10^{-1}$	$1.69 \times 10^{-1}$	$1.15 \times 10^{-1}$	$6.06 \times 10^{-2}$	$2.24 \times 10^{-2}$	$5.06 \times 10^{-3}$	$5.24 \times 10^{-4}$

for Co and Fe from Varas *et al.* [30]. The parameters of the Sutton-Chen potential for Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, Pb, and Al have been extracted from Rafii-Tabar and Sutton [31], and the parameters for Co from Kaszukur *et al.* [32]. We observe that for Ni the two-body expansion only explains about 20% of the interaction between the atoms in the cluster; while the three-, four-, and five-body interaction terms are similar in size. In this case a full multibody expansion of the Gupta potential is needed to account for the cluster properties. On the contrary, for Pt and Pd the two-body contribution amounts to about 70%, and the  $n$ -body interactions for  $n > 3$  may be disregarded.

A similar analysis is presented for the Sutton-Chen potential, and for the same elements shown in Fig. 8 and Table II. In this case we notice that the  $n$ -body contributions are similar for all elements, and that each of the  $n$ -body terms for  $n < 5$  contributes about 20% to the particle interactions. It is interesting to notice that the two descriptions of the same clusters provide different contributions to an  $n$ -body expansion, making one of them more suitable when truncating. Of course another issue is how good the expansion is, an issue which we discuss in the conclusions, where we also put forward a proposal on how to construct an  $n$ -body phenomenological potential from *ab initio* results.

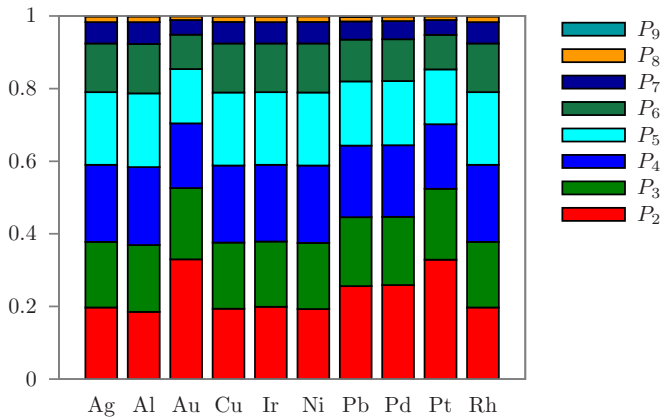


FIG. 8. Contribution of the  $n$ -body expansion for a nine-atom Sutton-Chen potential for different elements, obtained from  $M = 10^5$  different seeds.

Just as we can estimate the relevance of the  $n$ -body contribution for an  $N$  atom cluster, we can also determine the error due to the truncation of the potential by neglecting the higher  $m$ -body terms, with  $n \leq m \leq N$ . To do so we define

$$\varepsilon_m = \sqrt{\frac{1}{\alpha} \sum_{A \in C_N} \left( U(A) - \sum_{j=2}^m U_j(A) \right)^2}, \quad (15)$$

where the summation is over all clusters  $A \in C_N$  and the normalization factor is given by  $\alpha = \sum_{A \in C_N} U^2(A)$ . We could have used the expression given by Eq. (14), but for large clusters the summation over all subclusters takes significantly longer computer time. The results for the Gupta and Sutton-Chen potentials are shown in Figs. 9 and 10, respectively. We notice that for Au, Co, and Pt the Gupta potential seems to be reasonably well approximated by the two-body description, but the Sutton-Chen potential requires a higher  $n$ -body expansion. For  $N = 50$  we show the two-body contribution, as characterized by  $\varepsilon_2$ , for several elements of a relevant sector of the periodic table, illustrated in Fig. 11 for the Gupta potential and in Fig. 12 for the Sutton-Chen potential. Since the blue area corresponds to the value of  $\varepsilon_2$  for that element, the larger the blue area, the larger the relative

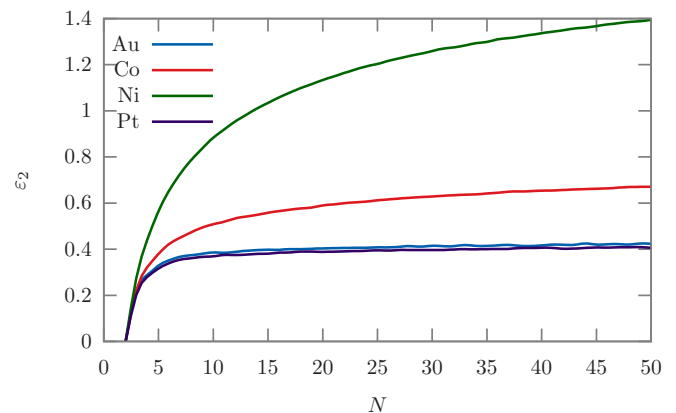


FIG. 9. Energy error when we use the two-body term to approximate the Gupta potential, using  $M = 10^5$  clusters of size  $N$  generated at random.

TABLE II. Contribution of the  $n$ -body expansion terms of nine-atom cluster using the Sutton-Chen potential. The data are obtained from  $M = 10^5$  clusters.

	$P_2$	$P_3$	$P_4$	$P_5$	$P_6$	$P_7$	$P_8$	$P_9$
Ag	$1.97 \times 10^{-1}$	$1.81 \times 10^{-1}$	$2.12 \times 10^{-1}$	$2.00 \times 10^{-1}$	$1.34 \times 10^{-1}$	$5.91 \times 10^{-2}$	$1.54 \times 10^{-2}$	$1.78 \times 10^{-3}$
Al	$1.85 \times 10^{-1}$	$1.84 \times 10^{-1}$	$2.15 \times 10^{-1}$	$2.03 \times 10^{-1}$	$1.36 \times 10^{-1}$	$6.00 \times 10^{-2}$	$1.56 \times 10^{-2}$	$1.80 \times 10^{-3}$
Au	$3.30 \times 10^{-1}$	$1.96 \times 10^{-1}$	$1.78 \times 10^{-1}$	$1.50 \times 10^{-1}$	$9.47 \times 10^{-2}$	$4.01 \times 10^{-2}$	$1.01 \times 10^{-2}$	$1.15 \times 10^{-3}$
Cu	$1.94 \times 10^{-1}$	$1.82 \times 10^{-1}$	$2.12 \times 10^{-1}$	$2.01 \times 10^{-1}$	$1.35 \times 10^{-1}$	$5.93 \times 10^{-2}$	$1.54 \times 10^{-2}$	$1.78 \times 10^{-3}$
Ir	$1.99 \times 10^{-1}$	$1.80 \times 10^{-1}$	$2.11 \times 10^{-1}$	$2.00 \times 10^{-1}$	$1.34 \times 10^{-1}$	$5.91 \times 10^{-2}$	$1.53 \times 10^{-2}$	$1.78 \times 10^{-3}$
Ni	$1.93 \times 10^{-1}$	$1.82 \times 10^{-1}$	$2.13 \times 10^{-1}$	$2.01 \times 10^{-1}$	$1.35 \times 10^{-1}$	$5.95 \times 10^{-2}$	$1.54 \times 10^{-2}$	$1.79 \times 10^{-3}$
Pb	$2.56 \times 10^{-1}$	$1.90 \times 10^{-1}$	$1.97 \times 10^{-1}$	$1.77 \times 10^{-1}$	$1.15 \times 10^{-1}$	$4.99 \times 10^{-2}$	$1.28 \times 10^{-2}$	$1.46 \times 10^{-3}$
Pd	$2.59 \times 10^{-1}$	$1.88 \times 10^{-1}$	$1.97 \times 10^{-1}$	$1.77 \times 10^{-1}$	$1.15 \times 10^{-1}$	$4.98 \times 10^{-2}$	$1.28 \times 10^{-2}$	$1.46 \times 10^{-3}$
Pt	$3.29 \times 10^{-1}$	$1.95 \times 10^{-1}$	$1.78 \times 10^{-1}$	$1.51 \times 10^{-1}$	$9.52 \times 10^{-2}$	$4.04 \times 10^{-2}$	$1.02 \times 10^{-2}$	$1.16 \times 10^{-3}$
Rh	$1.97 \times 10^{-1}$	$1.81 \times 10^{-1}$	$2.12 \times 10^{-1}$	$2.00 \times 10^{-1}$	$1.34 \times 10^{-1}$	$5.92 \times 10^{-2}$	$1.54 \times 10^{-2}$	$1.78 \times 10^{-3}$

error. Hence, in general even for  $N = 50$  there are a number of elements that when described by the Gupta potential may still allow a reasonable two-body description, within a certain error.

We see that in general we can expect that the  $n$ -body terms have a characteristic distance of action, because the  $n$ -body interactions are important only when the  $n$  atoms are close enough to each other. We recall that the  $n$ -body potential is defined so that it becomes small if any of the distances between the  $n$  atoms is large (i.e., larger than this characteristic distance). In Fig. 13 we show the relative contribution to the global minima of the  $(N - i)$ th body potential term, for stable clusters of size  $N$  using the Gupta potential. We notice that as  $N$  increases the  $(N - i)$ th contribution decreases. Of course, at the same time the number of minimum energy structures also increases with  $N$ , giving a distribution of the measure when calculated over all the minimum energy structures.

Similarly, we have calculated the relative error  $\sum_{i=2}^k |U_i - U|/U$  in the truncation of the  $n$ -body potential at a given order  $k$ , for a linear chain of  $N$  Gupta atoms placed at their equilibrium positions derived from the two-body potential. We see in Fig. 14 that the error quickly saturates to a small value for a small  $k$ , confirming the notion that there is a characteristic distance over which an  $n$ -body potential becomes negligible. Hence, we have shown that for  $n$  larger

than a certain  $n_0$  the characteristic distance of action of the  $n$ -body potentials becomes smaller than the size of every  $n$  atom subcluster, so that we can neglect  $n$ -body potentials for  $n > n_0$ . Hence, it is possible to estimate the contribution of each term in the  $n$ -body expansion, for a large cluster of size  $N$ , from all the relevant subclusters that are smaller than the  $n$ -body characteristic distance. This procedure can be applied to *ab initio* calculations to construct iteratively the  $n$ -body contribution (see comment at the end of the Conclusions) of each cluster.

More important, Fig. 14 shows an explicit determination and explanation of the empirical assumption that is commonly used when trying to fit a multibody potential, i.e., that it is possible to truncate the multibody expressions at 20 to 100 atoms to obtain reasonably accurate representations of the full potential. For example, Fig. 14 shows that, using neural networks to construct an empirical interaction potential in a large system, it is sufficient to consider three to four atoms to represent with reasonable accuracy the interactions

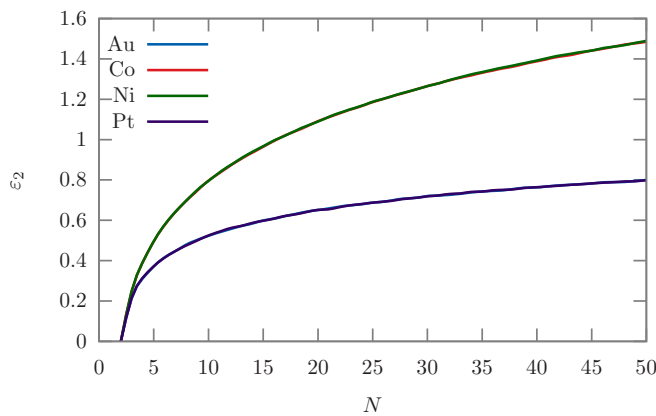


FIG. 10. Energy error when we use the two-body term to approximate the Sutton-Chen potential, for different elements, using  $M = 10^5$  clusters of size  $N$  generated at random.

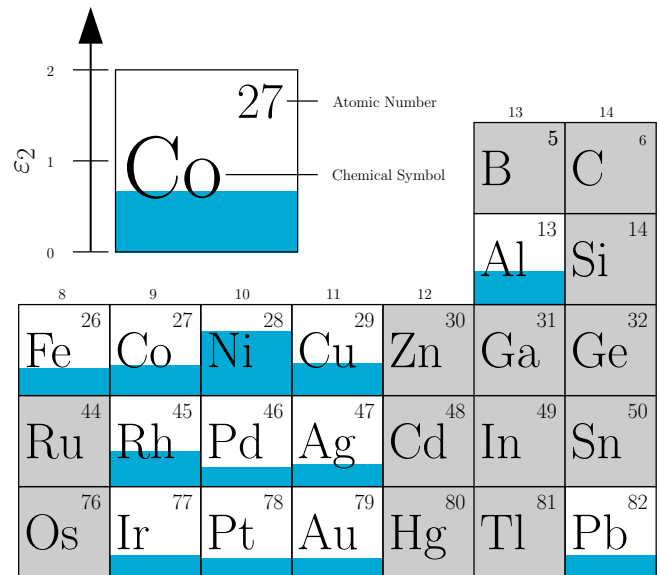


FIG. 11. Energy error when we use the two-body term to approximate the Gupta potential, for different elements, using  $M = 10^4$  clusters of size  $N = 50$  randomly generated. The blue area corresponds to the value of  $\epsilon_2$  for that given element.

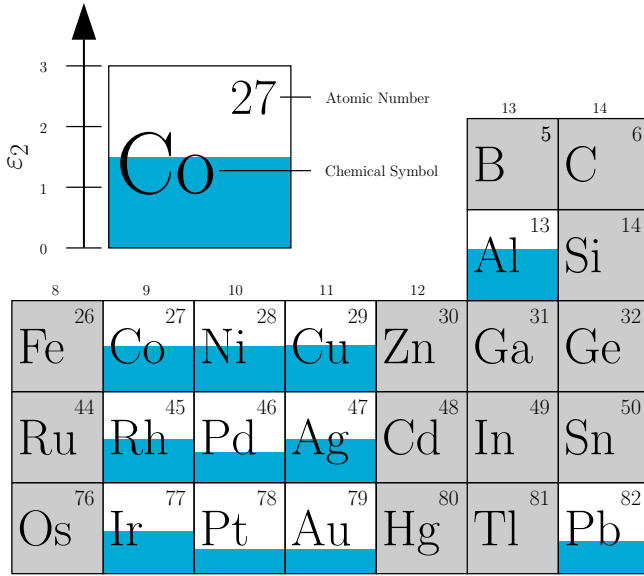


FIG. 12. Energy error when we use the two-body term to approximate the Sutton-Chen potential, for different elements, using  $M = 10^4$  clusters of size  $N = 50$  randomly generated. The blue area corresponds to the value of  $\epsilon_2$  for that given element.

of the atoms along a line. Therefore, not much is gained by including more atoms or a higher order term in the energy evaluation. When translating this to large systems we notice that it is necessary, at most, to consider between  $3^3 = 27$  to  $4^3 = 64$  atomic interactions when estimating the potential interaction of a large systems of atoms. Hence, this provides an explicit determination of the interaction order that has to be included when modeling large systems, for example using neural networks [5].

#### IV. DISCUSSION AND CONCLUSIONS

We have developed a procedure to expand a multibody potential in terms of  $n$ -body contributions that can be used as a basis to expand and approximate elaborate potentials. Besides

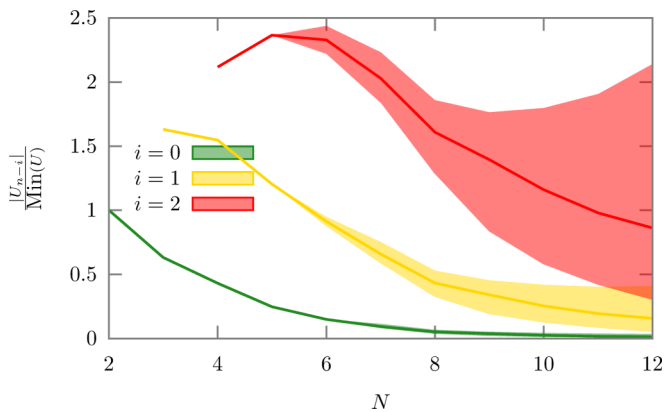


FIG. 13. Relative contribution  $|U_{n-i}|/|\text{Min}(U)|$ , relative to the global minima, of the  $(N - i)$ -body potential term for stable clusters of size  $N$ , using the Gupta potential. The distribution are given by the filled areas, and the averages by the lines.

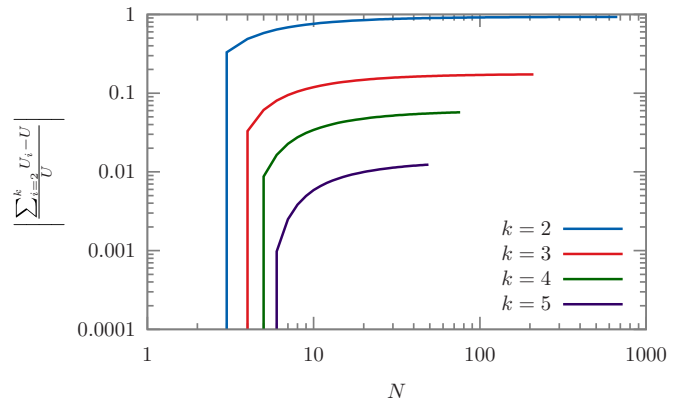


FIG. 14. The relative error  $\sum_{i=2}^k |U_i - U|/U$  in the truncation of the  $n$ -body potential at a given order  $k$  for a linear chain of  $N$  Gupta atoms placed at their equilibrium positions, derived from the two-body potential.

providing a method to assert “how many body” the effective interactions of the atoms in the cluster are, this strategy may help, for example, to search for a suitable set of cluster seeds to be further refined by *ab initio* methods. It is relevant to mention that more important than a very accurate approximation to the potential, it is desirable to produce a genuinely diverse set of structures to be refined, so that at the end a significant fraction of phase space is sampled in the search for the global minimum, or the distribution of the local minima. We have also studied the convergence and the error due to the truncation of such an expansion, which is controlled by a characteristic distance for a given  $n$ -body potential. This type of analysis may be useful when conducting molecular dynamic simulations.

Furthermore, this procedure allows us to estimate the relevance of every term of an  $n$ -body expansion of the potential energy, obtained from an *ab initio* approach, by computing iteratively the  $n$ -body contribution. This is similar to what is done by a multibody phenomenological approximation, but evaluating *ab initio* the energy contribution for each term of the expansion. A similar approach can be implemented by means of neural networks, which can be used to iteratively construct the  $n$ -body expansion of an *ab initio* potential. The truncation of the potential for an  $n$ -body expansion is absolutely necessary to implement the neural network approach, since the number of variables increases very rapidly with the number  $N$  of atoms in the cluster (i.e.,  $3N$ ), which soon becomes numerically unmanageable for large  $N$ . The exploration of these ideas is in progress.

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