Research paper

Iterative combining rules for the van der Waals potentials of mixed rare gas systems

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ARTICLE INFO

ABSTRACT

An iterative procedure is introduced to make the results of some simple combining rules compatible with the Tang-Toennies potential model. The method is used to calculate the well locations R_e and the well depths D_e of the van der Waals potentials of the mixed rare gas systems from the corresponding values of the homo-nuclear dimers. When the "sizes" of the two interacting atoms are very different, several rounds of iteration are required for the results to converge. The converged results can be substantially different from the starting values obtained from the combining rules. However, if the sizes of the inter-acting atoms are close, only one or even no iteration is necessary for the results to converge. In either case, the converged results are the accurate descriptions of the interaction potentials of the hetero-nuclear dimers.

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1. Introduction

The quest for reliable combining rules for predicting the parameters of the interaction potentials of the mixed systems from the parameters of the like systems has a long history [1–17]. Such rules have the obvious advantage that they can extend the data on a few like systems to a large number of unlike systems.

Most of such rules are empirical. To assess the accuracy of them, the interactions among the rare gas atoms are often used for comparison. This is due to the fact that as a result of a careful analysis of all the available data both experimental and theoretical, we are now in commend of a remarkably accurate knowledge of the potential energy curves of both the homogeneous and heterogeneous rare gas dimers [18–27].

Recently we proposed a novel way of using combining rules to determine the potential energy curves of the heterogeneous dimers of the group 2 (except Be) and group 12 (IIB) atoms from the data of the corresponding homogeneous dimers [28,29]. The results agree with experiments quite well.

The way is based on the assumption that the van der Waals potentials can be described by the Tang-Toennies potential model [30] which consists of an exponential repulsion and a damped dispersion attraction. The first step is to transform the homo-nuclear potential $V(R)$ into the reduced potential $U(x)$, defined as $U(x) = V$

$(x R_e)/D_e$, where $x = R/R_e$, R_e is the equilibrium distance and D_e is the well depth. Then combine the parameters of the two homo-nuclear reduced potentials into the parameters of the reduced hetero-nuclear potential with some simple combining rules. The idea is that the shapes of the reduced potentials are much closer to each other than the actual potentials. Combining rules applied to the reduced potentials should be more accurate. The last step is to use the well established combination rules for the dispersion coefficients and the range parameters of the repulsion to transform the reduced potential back into the actual hetero-nuclear potential. While the combination rules for the dispersion coefficients are accurate for all interactions, the combination rule for the range parameters may not be so accurate if the "sizes" of the interacting partners are very different (size as measured by the R_e of the homo-nuclear dimer). In such a case, the consistent check build in the method will indicate that the solution is not satisfactory. The present paper shows that these deficient solutions can be remedied by an iterative process so that a "self-consistent" result can be obtained for all systems.

In previous applications of this method, the "sizes" of the inter-acting atoms are not so different to require iteration. In this paper, we test this method on the rare gas dimers. Within the rare gas group, the difference in size between some interacting partners, such as He-Xe, can be very large. For such systems, several rounds of iteration are required for the results to converge. While for others, such as Kr-Xe, consistent result can be obtained with only one or no iteration. In either case, accurate potentials for the mixed systems can be generated from those of like systems.

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Atomic units will be used in all calculations. For comparison with literature values, one can convert energy unit to cm^{-1} and length unit to Å. For energy: 1 a.u. = 1 hartree = 2.19474×10^5 cm^{-1}; for distance: 1 a.u. = 1 a_0 = 0.52917 Å; for inverse distance: 1 a.u. = 1 a_0^{-1} = 1.88975 Å^{-1}.

2. Potential energy curves for the homo-nuclear rare gas dimers

The ground state potentials of the homo-nuclear dimers of rare gas can be described by the Tang-Toennies (TT) potential model [30]. In the TT potential model, the short-range repulsive Born-Mayer potential $A\exp(-bR)$ is added to the long-range attractive potential, which is given by the damped dispersion series, the model is

$$V(R) = Ae^{-bR} - \sum_{n=3}^{5} f_{2n}(bR)\frac{C_{2n}}{R^{2n}}, \tag{1}$$

where the C_{2n} are the dispersion coefficients. This equation was derived from a physical model and has a theoretical foundation [31]. The Born-Mayer range parameter b is the only parameter in the damping function $f_{2n}(bR)$,

$$f_{2n}(bR) = 1 - e^{-bR}\sum_{k=0}^{2n}\frac{(bR)^k}{k!}. \tag{2}$$

With a given set of dispersion coefficients, Eq. (1) depends on only the two parameters A and b. Conversely, the potential curve can also be uniquely determined from the values of the equilibrium distance R_e and the well depth D_e, through the requirements

$$V(R_e) = -D_e, \tag{3}$$

$$\left(\frac{dV(R)}{dR}\right)_{R=R_e} = 0. \tag{4}$$

There is a simple program in the Appendix of [14] which will automatically convert R_e and D_e into A and b.

In this paper, we will use the rare gas potentials described in [32] to illustrate the present method. The model parameters for the homo-nuclear rare gas dimers, determined in [32], are listed in Table 1. The shapes of these potentials are best studied by their reduced form. The reduced potential is obtained by setting

$$x = R/R_e, \tag{5}$$

$$U(x) = V(R_e x)/D_e. \tag{6}$$

So

$$U(x) = A^* e^{-b^* x} - \sum_{n=3}^{5}\left[1 - e^{-b^* x}\sum_{k=0}^{2n}\frac{(b^* x)^k}{k!}\right]\frac{C_{2n}^*}{x^{2n}}, \tag{7}$$

where

$$A^* = \frac{A}{D_e}, \tag{8}$$

$$b^* = bR_e, \tag{9}$$

$$C_6^* = \frac{C_6}{D_e R_e^6}, \tag{10}$$

$$C_8^* = \frac{C_8}{D_e R_e^8}, \tag{11}$$

$$C_{10}^* = \frac{C_{10}}{D_e R_e^{10}}. \tag{12}$$

The parameters of the reduced potentials for homo-nuclear rare gas dimers, calculated with the data listed in Table 1, are shown in Table 2. The potentials $V(R)$ are plotted in Fig. 1(a), and the reduced potentials $U(x)$ are plotted in Fig. 1(b). It is seen that the five potentials $V(R)$ are vastly different, but their reduced potentials $U(x)$ are very similar. In the scale of Fig. 1(b), these reduced potentials are not distinguishable. However, they are not identical, the differences between these reduced potentials are shown in Fig. 1(c).

3. Combining rules for potential parameters

Since the parameters of the reduced potentials of homo-nuclear rare gas dimers are very close to each other, as seen in Table 2, it is reasonable to assume that the parameters of the reduced potentials of the hetero-nuclear dimers are given by the following simple combining rules:

$$C_6^{*ij} = \left(C_6^{*i}C_6^{*j}\right)^{1/2}, \tag{13}$$

$$b_{ij}^* = \frac{1}{2}(b_i^* + b_j^*), \tag{14}$$

where a single index indicates the potential parameter for the like system and the double index refers to the combined system. These parameters of $U(x)$ of the mixed systems are listed in Table 3.

It is to be emphasized that Eqs. (13) and (14) are used only for the parameters of the reduced potentials $U(x)$. They may not be accurate for actual potential $V(R)$, but they can still be good approximations for the reduced potentials. For example, it is known that $C_6^{ij} \leq (C_6^i C_6^j)^{1/2}$ [33], the equal sign can be used if $C_6^i \approx C_6^j$ [34]. For the actual potential $V(R)$, the variation among C_6 can be as large as a factor of 200, whereas for the reduced potentials, the variation among C_6^* is within a factor of 2. Therefore, Eq. (13) for C_6^{*ij} is much more accurate than when it is applied to C_6^{ij}.

Eq. (14) is the consequence of

$$A_{ij}^* e^{-b_{ij}^* R} = \left(A_i^* e^{-b_i^* R} A_j^* e^{-b_j^* R}\right)^{1/2}. \tag{15}$$

In fact, the b^* values in Table 2 are so close, there is very little difference between the arithmetic and the geometric averages.

While $U(x)$ gives the shape of the potential, to determine the actual potential $V(R)$ we still need some information about the potential itself. Previously we have used the combining rules in [14] for the dispersion coefficients. These combining rules are based on the one term approximation of the dynamic polarizabilities [35] and are probably the most well established among all

Table 1
Parameters of the TT potential model for homo-nuclear rare gas dimers. All values are in atomic units.

System	A	b	C_6	C_8	C_{10}	R_e	D_e ($\times 10^{-4}$)
He-He	41.96	2.523	1.461	14.11	183.6	5.62	0.348
Ne-Ne	199.5	2.458	6.383	90.34	1536	5.84	1.34
Ar-Ar	748.3	2.031	64.30	1623	49,060	7.10	4.54
Kr-Kr	832.4	1.865	129.6	4187	155,500	7.58	6.38
Xe-Xe	951.8	1.681	285.9	12,810	619,800	8.25	8.96