Calculation of the van der Waals potential of argon dimer using a modified Tang-Toennies model

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Abstract. The Tang-Toennies (TT) potential model was modified based on the physical nature of the interatomic interaction to describe the Ar–Ar potential very accurately in the short range of the repulsive region. Using the modified TT potential model, the ground state van der Waals potential energy curve of Ar_2 was calculated. Compare to the experimental result, the current potential shows that the modified potential model not only gives the precise result in the long-range part, but also gives quite accurate result in the short-range repulsive part.

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1 Introduction

In recent years, with magneto-optical traps [1,2], a number of fields in ultracold atom physics, such as photoassociation [1,3], optical frequency standards [4,5], as well as possible Bose-Einstein condensates [6,7], have been initiated. The accuracy of interaction potentials is necessary for these investigations.

The interatomic potentials are also necessary in the studies of new materials, atomic and molecular collisions. Usually, *ab initio* method is used to calculate the van der Waals potential of dimers, but it is very complicated, time consuming and difficult to apply to complex systems, so a relatively simple and reliable method of calculation is necessary.

Tang-Toennies (TT) potential model [8] is a relatively simple analytic function. It has been used to calculate a lot of two-atom interaction potentials successfully, such as recently to the van der Waals potentials of mercury [9,10] and group IIA systems [11–13].

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In this paper, the repulsive part of the TT model is modified based on the physical nature of the interatomic interaction. This modified TT potential model (MTT) can describe entire part, especially the short-range repulsive part of Ar–Ar potential correctly.

2   Tang-Toennies potential model

In 1984, Tang and Toennies [8] proposed a potential model which consists of the sum of the short range repulsive Bon-Mayer potential Ae^{-bR} and the long range attractive potential of the damped asymptotic dispersion series

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

where R is the internuclear distance, A and b are the parameters of the Born-Mayer repulsive potential, C_{2n} are the dispersion coefficients, and $f_{2n}(bR)$ is the damping function

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

For many systems, the first three coefficients C_6, C_8 and C_{10} are available, higher accuracy additional terms can be generated by the recurrence relation

$$C_{2n} = \left(\frac{C_{2n-2}}{C_{2n-4}}\right)^3 C_{2n-6}. \tag{3}$$

3   The modified Tang-Toennies potential model

In 1995, K. T. Tang [14] obtained an exchange energy for two-atom systems based on a surface integral method [15]. This method calculates the exchange energy by a surface integral which accounts for the flux of electrons flowing from one atom to another. The analytical expression of this exchange energy is $TR^{7/2\beta-1}e^{-2\beta R}$, where T is the amplitude of the atom wave function, it may be calculated by a highly accurate CI calculation, $\beta = \sqrt{2\epsilon}$, with ϵ is the ionization energy of the atom. Since the exchange energy is the mainly contribution to the repulsive potential, we found that using $TR^{7/2\beta-1}e^{-2\beta-1}e^{-2\beta R}$ to replace $A\exp(-br)$ in the TT model and adjusting T and β by the experimental well depth and equilibrium distance R_e, the entire ground state potential curve of the argon dimer can be accurately described. We call this modified TT potential model as MTT model, that is

$$V(R) = TR^{7/2\beta-1}\exp(-2\beta R) - \sum_{n\geq3}^{N_{\max}} \left(f_{2n}(bR)\right) \frac{C_{2n}}{R^{2n}}, \tag{4}$$

where

$$b = 2\beta - \frac{\frac{7}{2\beta} - 1}{R}.$$ (5)

In the MTT potential model, there are five essential parameters: T, β, C_6, C_8 and C_{10}. If the first three dispersion coefficients C_6, C_8 and C_{10} are available only two parameters (T, β) need to be known in order to use the MTT model. Furthermore, if the equilibrium distance R_e and the well depth of the potential D_e are known, then parameters T and β can be determined from Eq. (4) [16].

4   Calculation of the potential of Ar$_2$ using MTT model

In principle, the dispersion series in Eqs. (1) and (4) should include all the terms necessary for convergence, but in our applications, with the well depth D_e and equilibrium distance R_e well established by experiment, the errors from the high order dispersion terms can be compensated by changes in the short range parameters T and β. In this work, dispersion series is set at $N_{\max} = 5$.

For Ar$_2$, $D_e = 0.000454$ a.u. and $R_e = 7.10$ a.u. were well established by Aziz *et al.* [17]. Together with the *ab initio* calculated three dispersion coefficients $C_6 = 64.3$ a.u. [18], $C_8 = 1623$ a.u. [19], and $C_{10} = 49060$ a.u. [19], T and β were determined from Eq. (4), and the Born-Mayer parameters A and b [20] were determined from Eq. (1). All parameters are listed in Table 1.

Table 1: The parameters of MTT and TT models for Ar–Ar dimer, all values are in atomic units.

C_6	C_8	C_{10}	R_e	D_e	T	β	A	b
64.30	1623	49060	7.10	4.54×10^{-4}	96.1149	1.1523935	748.3	2.031

Table 2: Comparison of the argon dimer potentials of MTT and TT models with the experimental potential. All values are in atomic units.

R	Exp. [21]	Present				
	$V_{\mathrm{Exp.}}(R)$	$V_{\mathrm{MTT}}(R)$	$(V_{\mathrm{MTT}} - V_{\mathrm{Exp}})/V_{\mathrm{Exp}}$	$V_{\mathrm{TT}}(R)$	$(V_{\mathrm{TT}} - V_{\mathrm{Exp}})/V_{\mathrm{Exp}}$
3.21258	0.59018	0.5909016	0.001222678	1.010776	0.712657155
3.40155	0.41185	0.4228865	0.026797378	0.680173	0.651506616
3.59053	0.28737	0.3001823	0.044584682	0.456778	0.589511779
3.7795	0.20052	0.2113449	0.053984141	0.306013	0.526097147
3.96848	0.13992	0.1475851	0.054782018	0.204392	0.460777587
4.15745	0.09764	0.1022018	0.046720606	0.136013	0.393004916
4.34643	0.06816	0.07014507	0.02912368	0.090086	0.321684272
4.5354	0.04757	0.04767430	0.002192558	0.059315	0.246899306
4.72438	0.03318	0.03203939	-0.03437643	0.038755	0.168022905
5.00784	0.01934	0.01719695	-0.1108092	0.020064	0.037435367

The ground state potentials of argon dimer were calculated using the MTT and TT models with parameters listed in Table 1. Results are shown in Figs. 1 and 2, the experimental results [21, 22] are also shown for comparison. It can be seen from that in the long and well regions, the MTT model potential and the TT model potential are coincide and they are in excellent agreement with the experimentally determined potential. But in the short range ($R < 6.0$ a.u.), the TT potential are too stiff and only the MTT model potential energy curve is in good agreement with the experimental result. The numerical values of differences between theoretical potentials and the experimental potentials are listed in the Table 2.
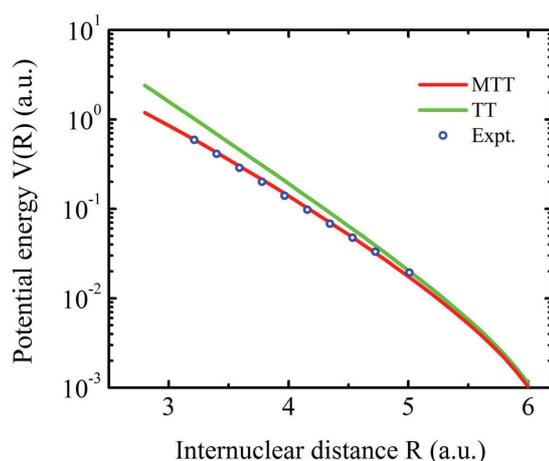

Figure 1: The van der Waals potentials of Ar–Ar in short-range region. Red line: present work; green line: TT model potential; empty circle: experimental result [21].
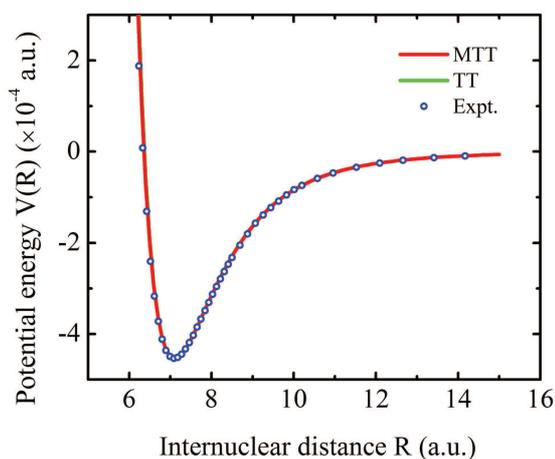

Figure 2: The van der Waals potentials of Ar–Ar. Red line: present work; green line: TT model potential; empty circle dot: experimental result [22].

As seen in Table 2, in the repulsive part of the potentials, the largest difference between the present MTT value and the experimental value is only 5.478% at 3.97 a.u. So the modified TT potential model can describe the entire potential curve of Ar_2 very well.

5   Conclusion

The potential model proposed by Tang and Toennies is an excellent model for van der Waals systems and it has been successfully used for the systems of rare gas [23], group IA [24,25], group IIA [11–13] and group IIB [9,10]. But for the argon dimer, the modified TT potential model is more suitable to describe its van der Waals potential, especially in the short range repulsive region. This is because the exchange energy is the main contribution to the repulsive potential.

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