Eur. Phys. J. D **33**, 43–48 (2005)
DOI: 10.1140/epjd/e2005-00034-8

THE EUROPEAN PHYSICAL JOURNAL D

Ab initio study for the intermolecular interaction potential surface of Ar-N_2 complex

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Received 19 October 2004 / Received in final form 17 November 2004

Abstract. The intermolecular interaction potentials of van der Waals Ar-N_2 complex have been studied by ab initio calculations using the single and double excitation coupled cluster [CCSD(T)] theory with perturbative triples correction. The full counterpoise method is applied to correct the basis set superposition error (BSSE). It is found that the T-shaped structure is the most stable conformation with the well depth D_e of 12.40 meV at the minimum distance R_m of 3.70 Å. The calculated anisotropic values for ΔR_m, ΔR_0 and ΔD_e are 0.56 Å, 0.54 Å and 2.68 meV, respectively. Compared with those obtained by others, our calculated PES seems to be in better agreement with experiments.

PACS. 34.20.Gj Intermolecular and atom-molecule potentials and forces – 31.15.Ar Ab initio calculations

1 Introduction

It is well-known that the nonbonding interaction potentials, mainly resulting from van der Waals (vdW) interactions [1], play a crucial role to understand the structures and properties of gases, liquids, solids, as well as any other materials in condensed phase. Experimentally, the structures of numerous nonbonding interaction systems have been recently examined [2,3], however, it is difficult to confirm the nonbonding interaction potentials only from the experimental measurements [4], An effective way to obtain the information for the vdW systems is to carry out quantum chemical calculations with some suitable approximations [5,6]. The calculation of accurate intermolecular potential requires the use of large basis set along with a high level of electron correlation [7,8], In addition, the basis-set superposition error (BSSE) should be taken into account.

The interaction of a rare gas atom with a diatomic molecule represents a type case of the anisotropic interaction. To understand the gases equation of state, energy disposal in the chemical reactions, etc., it is important to know the involved nonspherical potential energy surface (PES). Moreover, once the potential surface is given, all the necessary physical observables could be calculated in principle. Therefore, many experimental [9,10] and theoretical [11,12] efforts have been devoted towards the characterization of the possible PESs.

Of all the various systems with vdW interactions, the accurate determination of the interactions of N_2 molecule with noble gas atoms has proven to be a challenging problem. The He-N_2 interaction can be characterized quite well [13] with only a few minor refinements. Furthermore, the Ne-N_2 potential has also been carefully analyzed [14] and the final PES chosen was found to describe the existing experimental data quite well. Here, we focus on Ar-N_2 complex, and make a calculation to the intermolecular potential surface of it using ab initio single, double excitation coupled cluster [CCSD(T)] theory with perturbative triples correction without any empirical adjustment and extrapolation procedure. Dham et al. [15] presented an exchange-Coulomb model PES (XC3) by fitting the Heitler-London interaction energy, long-range dispersion energies, the temperature dependencies of interaction second virial, binary diffusion, and mixture shear viscosity coefficients, microwave spectra, as well as the collision broadening of the depolarized Rayleigh light scattering spectrum. Compared to previous potentials [16–19], this XC3 potential gave the best overall agreement with the experiment. However, as pointed out by the authors, further improvement in the anisotropic part of this PES is required to obtain a better agreement with the relaxation cross sections. Later, Wang et al. [20] performed quantum mechanical calculations of the Ar-N_2 IR spectrum to test the XC3 [15] and MMSV2 [21] potential surfaces. Recently, Fernández et al. [22] and Patel et al. [23] both group made high-level ab initio calculations to the intermolecular potential surfaces of Ar-N_2 system by the

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Table 1. Counterpoise corrected values of intermolecular interaction energies (in meV) for Ar-N_2 ($R = 3.68$ Å and $\theta = 90°$) at the SCF and correlated [MP2, CCSD and CCSD(T)] levels using the different basis sets. N_b is the number of basis functions.

Basis set	N_b	SCF	MP2	CCSD	CCSD(T)
cc-pVDZ	46	12.09275	3.04496	5.76610	5.12119
cc-pVTZ	94	12.36486	–5.12119	0.28300	–1.43404
aug-cc-pVDZ	73	12.68323	–8.51717	–3.05856	–5.31983
aug-cc-pVTZ	142	12.80024	–12.7594	–6.26679	–9.57025
aug-cc-pVDZ+BF[a]	102	12.77303	–14.5554	–8.92262	–12.3458
cc-pVTZ+BF	123	12.74582	–14.4683	–7.88858	–11.3526
aug-cc-pVTZ+BF	171	12.88460	–15.0642	–8.32669	–12.0683

[a] BF denotes the midbond functions $3s3p2d1f$ from reference [25].

same method as our. However, they employed empirical procedures to improve their PES representation. Moreover, Patel et al. [23] made use of a basis set extrapolation scheme, and thus were able to obtain a good agreement with experimental microwave transition frequencies for the Ar-N2 complex.

In this work, the full counterpoise method is applied to correct for the basis set superposition error (BSSE). A dimensional complete ab initio CCSD(T) intermolecular potential surface containing 161 points for Ar-N_2 is presented. It is found that the T-shaped structure is the most stable conformation with the well depth D_e of 12.40 meV at the minimum distance R_m of 3.70 Å. The calculated anisotropic values for ΔR_m, ΔR_0 and ΔD_e are 0.56 Å, 0.54 Å and 2.68 meV, respectively. Compared with those obtained by others [15–19,21–23], our calculated PES seems to be in better agreement with experiments.

2 Theoretical method

The intermolecular interaction energies for Ar-N_2 system are computed using ab initio single and double excitation coupled cluster theory with perturbative triples correction [CCSD(T)] [24] in the framework of the supermolecule method, in which the interaction energies are obtained simply as differences between the energies of the complex (AB) and the monomers (A and B), i.e.

$$\Delta E = \overline{E}_{AB} - \overline{E}_A - \overline{E}_B. \qquad (1)$$

We first carry out a convergence study and establish an efficient basis set, referred to hereinafter as aug-cc-pVDZ+BF, which consists of two sections. One is the augmented correlation consistent double zeta basis set used for Ar and N atoms, the other is the bond functions set ($3s3p2d1f$) defined by Tao and Pan [25], The bond functions are placed on the midpoint of the vector $\boldsymbol{R}$ joining Ar with the center-of-mass of N_2 molecule.

The full counterpoise (CP) method is applied to correct the basis set superposition error (BSSE) [26]. The basis set for the complex is used for the calculations of the monomer energies with appropriate nuclear charges set to zero. The bond length of N_2 is fixed at its equilibrium value of 2.068 a.u. The geometry of the complex is specified by the magnitude $|\boldsymbol{R}|$ and the angle θ between $\boldsymbol{R}$ and the axis of N_2. All the calculations are carried out using Gaussian03 program [27].

3 Results and discussion

To choose a best size-performance ratio basis set, we first carry out a convergence study on the Ar-N_2 complex. We start with cc-pVDZ basis set and the effect of further increasing the basis set is tested using the cc-pVTZ basis set. Then, we augmented the two basis sets to the aug-cc-pVDZ and aug-cc-pVTZ level, respectively. We also consider the use of midbond functions [25]. Using these basis sets, we obtained the counterpoise corrected interaction energies of Ar-N_2 at $R = 3.68$ Å and $\theta = 90°$, which are listed in Table 1.

Table 1 is separated into two groups. The first group (first 4 entries) is from the calculations using the purely atomic basis sets. The first basis set cc-pVDZ yields only intermolecular interaction energy ΔE of 5.12119 meV at the CCSD(T) level and the much smaller electron correlation energy, corresponding to the difference between the SCF energy and the energy obtained with electron correlation, –6.97156 meV. Compared with the results obtained from cc-pVDZ basis set, the cc-pVTZ basis set improves the electron correlation energy about 98%. The aug-cc-pVTZ presents the electron correlation energy about –22.4 meV, which increases as much as 24.3% compared with the results obtained from aug-cc-pVDZ at CCSD(T) level. Therefore, we find the diffuse polarization functions are favorable for intermolecular interaction energy. It is clear that the intermolecular interaction energy from the purely atomic basis sets converges very slowly with the augmentation of basis set, and is far away from the empirical values –13.2 meV of MMSV potentials [18].

The second group (last three entries) is from the calculations using the bond function basis sets (the atomic basis sets augmented with the bond functions). The interaction energy and electron correlation energy yielded by aug-cc-pVDZ+BF basis set (only 102 basis functions) are about –12.35 meV and –25.12 meV, respectively, which are improved about 29% and 12.3% compared with those yielded by the largest pure atomic basis set aug-cc-pVTZ (with 142 basis functions). Particularly, the interaction energy and electron correlation

Table 2. CCSD(T) interaction energies (in meV) for Ar-N_2.

R/Å	$\theta = 90°$	75°	60°	45°	30°	15°	0°
2.50	570.2666	642.2407	889.6903	1381.115	2126.922	2919.016	3284.729
2.75	205.2202	236.331	344.9752	563.4365	893.1054	1232.562	1383.613
3.00	59.59841	72.16191	116.8975	208.3604	346.8964	488.1997	550.141
3.25	6.36747	10.94443	27.90801	63.85155	119.1587	175.6033	200.1208
3.50	–9.80155	–8.48996	–3.03951	9.67637	30.27812	51.56016	60.71952
3.75	–12.3948	–12.2533	–11.1567	–7.60014	–0.91158	6.34298	9.45868
4.00	–10.724	–10.9145	–11.2029	–10.8873	–9.4097	–7.46953	–6.6287
4.25	–8.21512	–8.45458	–9.05323	–9.66821	–9.89407	–9.7825	–9.71991
4.50	–5.99739	–6.2042	–6.77292	–7.51307	–8.15254	–8.54438	–8.69676
4.75	–4.31029	–4.47628	–4.92798	–5.55929	–6.17971	–6.62325	–6.79197
5.00	–3.1021	–3.22183	–3.56197	–4.04089	–4.53614	–4.90349	–5.03955
5.25	–2.25583	–2.3429	–2.58508	–2.93339	–3.30074	–3.57286	–3.67354
5.50	–1.66262	–1.7252	–1.89663	–2.14426	–2.40549	–2.60141	-2.66944
5.75	–1.24628	–1.28982	–1.40955	–1.58642	–1.76874	–1.9048	–1.9565
6.00	–0.94424	–0.97417	–1.06397	–1.18642	–1.31703	–1.41499	–1.44765
6.25	–0.72654	–0.74831	–0.8109	–0.9007	–0.99049	–1.06124	–1.08573
6.50	–0.566	–0.58505	–0.62858	–0.69117	–0.75648	–0.80546	–0.82451
6.75	–0.44627	–0.45987	–0.48981	–0.53606	–0.58232	–0.6177	–0.6313
7.00	–0.35375	–0.36191	–0.38912	–0.41906	–0.45443	–0.47892	–0.48981

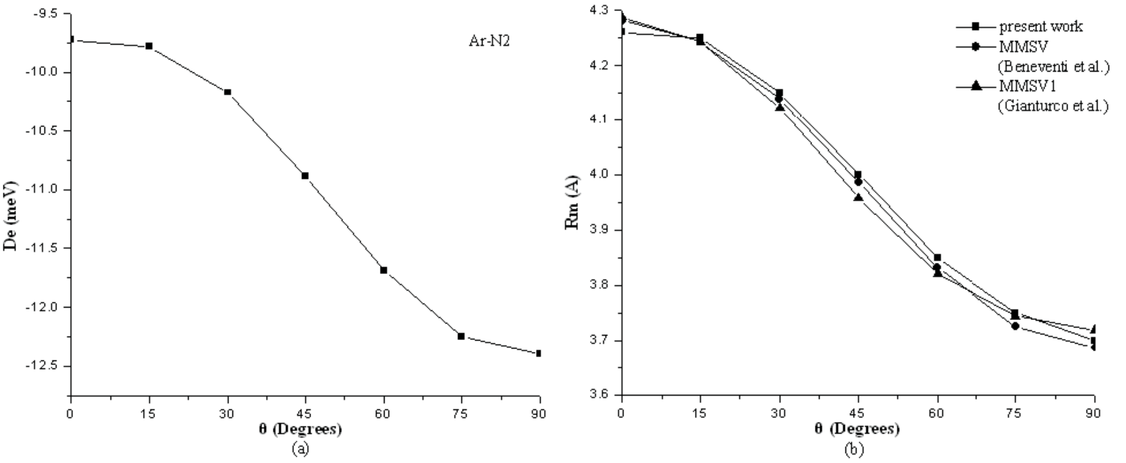
energy are improved only about 6.3% and 3.5%, respectively, from cc-pVTZ+BF (with 123 basis functions) to aug-cc-pVTZ+BF (with 171 basis functions). They are overestimated slightly about 2.3% and 0.6% from aug-cc-pVDZ+BF (with 102 basis functions) to aug-cc-pVTZ+BF (with 171 basis functions). All analysis above is based on CCSD(T) level. It is found that, although the aug-cc-pVDZ+BF basis set overestimates the property more slightly than the aug-cc-pVTZ+BF basis set, this basis set has the best size-to-performance ratio. Therefore, we think that this basis set is more suitable for applying to our other calculations.

It is clear that the use of bond functions could improve drastically the rate of convergence for the calculated interaction energy. In addition, when considering all the basis set sequences, we find that the MP2, CCSD and CCSD(T) interaction energies converge slowly as the number of basis functions increases, whereas the SCF interaction energy converges rapidly. The contrast between the SCF and MP2, CCSD and CCSD(T) energies results from that the atom-centered basis sets are almost saturated with respect to the SCF interaction energy, but are lacking higher polarization functions important for the dispersion forces that arise through electron correlation. Near saturation of the atom-centered basis set at SCF level is a prerequisite for the reliable use of bond functions.

In Table 2, we present the counterpoise corrected ab initio CCSD(T) interaction energies at 133 conformations corresponding to nineteen intermolecular distances R at each of seven angles θ. Table 3 lists the CCSD(T) interaction energies at 28 other geometries near the distances $R_m(\theta)$, at which the CCSD(T) potential is lowest for a fixed angle. Both Tables 2 and 3 present a considerably full description of the intermolecular interaction

Table 3. The CCSD(T) interaction energies for Ar-N_2 (units in meV).

θ	R/Å	$\Delta E(R,\theta)$/meV
90°	3.60	–11.7472
	3.65	–12.1989
	3.70	–12.3975
	3.80	–12.2451
75°	3.65	–11.7390
	3.70	–12.1172
	3.80	–12.2098
	3.85	–12.0193
60°	3.80	–11.5404
	3.85	–11.6873
	3.90	–11.6546
	3.95	–11.4805
45°	3.90	–10.4573
	3.95	–10.7757
	4.05	–10.8356
	4.10	–10.6560
30°	4.10	–10.1172
	4.15	–10.1716
	4.20	–10.0845
	4.30	–9.63011
15°	4.15	–9.56481
	4.20	–9.75801
	4.30	–9.67909
	4.35	–9.48589
0°	4.20	–9.60290
	4.26	–9.72535
	4.27	–9.72263
	4.28	–9.71991



(a) (b)

Fig. 1. (a) Angular dependence of the well depth D_e and (b) angular dependence of the potential minimum R_m, compared with the multiproperty-fit potential MMSV of Beneventi et al. [18] and the MMSV1 modified potential of Gianturco et al. [19].

potential surface for Ar-N_2 complex, referred to hereinafter as CCSD(T) surface. Figures 1a and 1b show how the well depth D_e and the corresponding equilibrium minimum distance R_m vary with orientation angle θ for our CCSD(T) surface, respectively.

It is shown from our calculated results that the T-shaped structure is the most stable conformation for Ar-N_2 complex, with a well depth D_e of 12.40 meV at a minimum distance R_m of 3.70 Å. These results agree well with those from an initial analysis of the purely rotational spectrum experiment, which has been measured using a molecular beam cavity microwave Fourier transform spectrometer for Ar-N_2 van der Waals complex [28].

A comparison for the anisotropies of the various surfaces is instructive. One commonly employed means for characterizing the anisotropy of a potential energy surface is to tabulate values of the main characteristics of the PES, which are the well position $R_m(\theta)$, well depth $D_e(\theta)$, and the crossing point $R_0(\theta)$ at the linear (L) and T-shaped geometries, respectively. Added to them are also the corresponding three anisotropy measurements, $\varDelta D_e$, $\varDelta R_m$ and $\varDelta R_0$, which are defined respectively as $\varDelta D_e = D_e(\mathrm{L}) - D_e(\mathrm{T})$, $\varDelta R_m = R_m(\mathrm{L}) - R_m(\mathrm{T})$ and $\varDelta R_0 = R_0(\mathrm{L}) - R_0(\mathrm{T})$, where L and T denote the linear- and T-shaped structures, respectively. In Table 4, we make a comparison of $D_e(\theta)$, $R_m(\theta)$, $R_0(\theta)$ for $\theta = 0°$ and 90°, and $\varDelta D_e$, $\varDelta R_m$ and $\varDelta R_0$ for our CCSD(T) surface, together with those obtained by others [15–19,21–23]. Cuts of the BTT, MMSV and CCSD(T) PES at linear (L) and T-shaped geometries are shown in Figure 2. In addition, the angle dependence of minimum equilibrium distance of multiproperty-fit MMSV surface, and MMSV1 modified surface is shown in Figure 1b compared with one of the CCSD(T) surface. All surfaces in Table 4 predict the T-shaped structure to be the most stable one, which agrees well with the microwave spectrum experiment studies [21, 28]. The main features of the calculated CCSD(T) potential are in good agreement with all of the existing potentials for Ar-N_2 in generally.

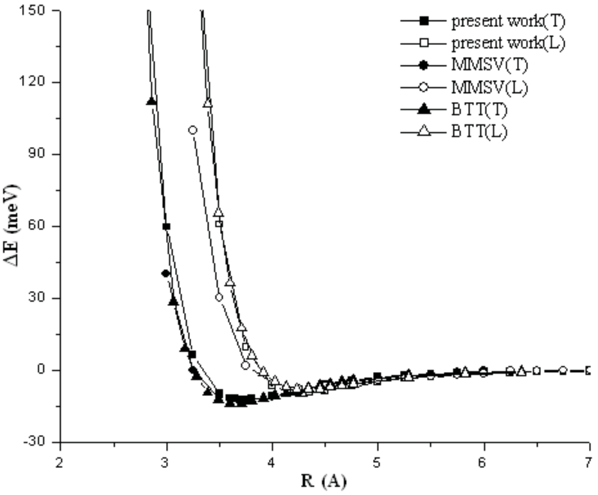


Fig. 2. The counterpoise corrected CCSD(T) anisotropic potential for linear (L) and T-shaped conformations, compared with the semiempirical BTT potential of Bowers et al. [17] and with the multiproperty-fit MMSV potential of Beneventi et al. [18] at the same geometries.

We find that, compared with the new exchange-Coulomb model potential XC3 [15], the empirical multiproperty fit surface MMSV [18], and its two modified potentials, i.e. MMSV1 [19] and MMSV2 [21], our ab initio CCSD(T) potential not only recovers their empirical well depths with sufficiently high accuracy (about 98%, 94%, 94% and 94% respectively), but also properly reproduces those empirical potential minimum positions. Tao et al. [25] pointed that for a routine calculation of the true van der Waals molecule, a 90% accuracy of the calculated binding energy was considered as a very favorable standard. Our calculation has evidently reached the high-quality level.

The $\varDelta R_m$ values given by MMSV potential and MMSV1 modified potential were 0.6 Å and 0.57 Å, respectively, while the present CCSD(T) potential makes

Table 4. Comparison of potential well parameters for Ar-N$_2$ complex.

	CPV[a]	BTT[b]	MMSV[c]	MMSV1[d]	MMSV2[e]	XC3[f]	rA PES[g]	MTE[h]	This work
R_m(L)/Å	3.96	4.31	4.28	4.29	4.33	4.37	4.242	4.26	4.26
D_e(L)/meV	8.77	8.16	7.55	7.55	7.55	7.05	9.67	9.93	9.73
R_0(L)/Å	3.55	3.86	3.81	3.81	3.84	3.90	3.86	3.86	3.86
R_m(T)/Å	3.57	3.65	3.68	3.72	3.71	3.726	3.696	3.70	3.70
D_e(T)/meV	12.75	13.90	13.20	13.20	13.20	12.71	12.596	12.993	12.398
R_0(T)/Å	3.20	3.23	3.27	3.27	3.30	3.30	3.28	3.3	3.32
ΔR_m/Å	0.39	0.66	0.60	0.57	0.62	0.64	0.546	0.56	0.56
ΔD_e/meV	3.98	5.74	5.65	5.65	5.65	5.66	2.93	3.06	2.68
ΔR_0/Å	0.35	0.63	0.54	0.54	0.54	0.60	0.58	0.56	0.54

[a] Empirical spherical average potential surface by Candori et al. (from Ref. [16]). [b] Semiempirical model surface by Bowers et al. (from Ref. [17]). [c] Multiproperty fit surface by Beneventi et al. (from Ref. [18]). [d] Modified potential from the PES of MMSV by Gianturco et al. (from Ref. [19]). [e] Refined potential from the PES of MMSV by Jäger et al. (from Ref. [21]). [f] Exchange-Coulomb model potential by Dham et al. (from Ref. [15]). [g] Modified ab initio fitted analytic PES by Fernández et al. (from Ref. [22]). [h] Modified Truhlar extrapolation ab initio fitted analytic PES by Patel et al. (from Ref. [23]).

the ΔR_m further slightly reducing to 0.56 Å. The rather small ΔR_m change should leave all the transport properties, which could be calculated via the CCSD(T) PES, essentially the same as those given by the previous work [18]. ΔR_0 is a good measure of the anisotropy of the low repulsive wall. Table 4 and Figure 2 show that the CCSD(T) surface and the empirical multiproperty fit surface MMSV together with its two modified potentials have the same ΔR_0values of 0.54 Å.

It is evident that the features of our CCSD(T) PES for Ar-N$_2$ are in agreement with the two ab initio surfaces, i.e. rA PES of Fernández et al. [22] and MTE of Patel et al. [23] This agreement is highly encouraging since it is well known that the two PESs can precisely predict the microwave transition frequencies within 0.1 MHz and 0.1% of the experimental values respectively. However, in order to obtain those levels of agreement between experiment and theory, the ab initio potential of Fernández et al. was modified slightly to fit the microwave data. Before this modification, the transition frequencies were predicted with a significantly larger error (100 MHz) owing to the equilibrium separation between Ar and N$_2$ being too large; on the other hand the complete ab initio potential of Patel et al. was extrapolated employing modified Truhlar basis set extrapolation procedure to estimate the complete basis set limit. But it is noted that the features of our ab initio CCSD(T) PES are in good agreement with the results of the high level modified ab initio potentials at the same level of theory with smaller basis set (102 basis functions against 171 basis functions of Fernández et al.), and without any empirical adjustment or basis set extrapolation procedure are employed.

All the ab initio potentials for Ar-N$_2$ system predict a significantly smaller anisotropy in the well depth than those derived from all the semiempirical potentials. The CCSD(T) surface has the smallest anisotropy in the well depth for reasons that are not entirely clearly to us. However, we can conclude that the ab initio CCSD(T) calculation with the bond functions in our basis set provides a good description of Ar-N$_2$ complex that is more accurate for the linear geometry than for the T-shaped structure. And the smaller anisotropy predicted by ab initio potentials is in closer agreement with the experimentally observed behavior of Ar-N$_2$ [23]. Figure 2 shows that the CCSD(T) potential has the same long-range dispersion part of the BTT potential and the MMSV potential.

4 Summary

In summary, we have made a calculation to the intermolecular potential surface for van der Waals Ar-N$_2$ complex using ab initio single, double excitation coupled cluster [CCSD(T)] theory with perturbative triples correction without any empirical adjustment and extrapolation procedure. We have investigated the orientations and intermolecular distances dependence of interaction energies for this complex. A dimensional ab initio CCSD(T) intermolecular potential surface containing 161 points for Ar-N$_2$ has been presented. It is found that the T-shaped structure is the most stable conformation with the well depth D_e of 12.40 meV at the minimum distance R_m of 3.70 Å. The calculated anisotropic values for ΔR_m, ΔR_0 and ΔD_e are 0.56 Å, 0.54 Å and 2.68 meV, respectively. Compared with those obtained by others, our calculated PES seems to be in better agreement with experiments.

The authors would like to acknowledge support for this work by the National Natural Science Foundation of P.R. China under Grant No. 60436010, and by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry under Grant No. 2004176-6-4.

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