

# AM1\* parameters for gold

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**Abstract** We report the parameterisation of AM1\* for gold. The basis set for gold contains one set each of *s*-, *p*- and *d*-orbitals. AM1\* parameters are now available for H, C, N, O and F (which use the original AM1 parameters), Al, Si, P, S, Cl, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Zr, Mo, I and Au. The performance and typical errors of AM1\* for gold are discussed.

**Keywords** AM1\* · Gold parameters · NDDO · Semiempirical MO theory

## Introduction

AM1\* [1–7] is an extension of AM1 [8] that uses *d*-orbitals for the elements P, S, Cl [1], Al, Si, Ti and Zr [2], Cu and Zn [3], Br and I [4], V and Cr [5], Co and Ni [6], Mn and Fe [7]. The AM1\* molybdenum parameters are a slight modification of Voityuk and Rösch's AM1(d) parameter set [9]. AM1\* retains the original AM1 parameters for the elements H, C, N, O and F. The intention is to provide a technique that has the advantages of AM1 for first-row elements, such as good energies for hydrogen bonds, higher rotation barriers for  $\pi$ -systems than MNDO [10, 11] or

PM3 [12–14], but that performs better for heavier elements and can be applied to transition metals. As a continuation of this work, new AM1\* parameters for gold are now reported. Gold is important in the chemistry of catalysts, and also has a very promising future in biochemical and biomedical applications [15, 16]. Because experimental data on heats of formation of compounds of gold are relatively sparse, we have also used a series of model compounds whose heats of formation were from DFT calculations [17].

## Theory

AM1\* for the new element gold uses the same basic theory as outlined previously [1, 2]. As for other element–H interactions, the core–core repulsion potential for the Au–H interaction used a distance-dependent term  $\delta_{ij}$ , rather than the constant term used for core–core potentials for most other interactions in AM1\* [1]. This distance-dependent  $\delta_{ij}$  was also used for the Mo–H and interaction in AM1(d) [8] and for Ti–H, V–H, Cr–H, Co–H, Ni–H, Cu–H, Zn–H, Br–H, Zr–H, Mo–H and I–H in AM1\* [2–7]. The core–core term for Au–H is thus:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 [1 + r_{ij} \delta_{ij} \exp(-\alpha_{ij} r_{ij})] \quad (1)$$

where all terms have the same meaning as given in reference [1].

In addition, the standard MNDO/d formula is used for all other core–core interactions:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 [1 + \delta_{ij} \exp(-\alpha_{ij} r_{ij})] \quad (2)$$

The parameterisation techniques were those reported in references [1] and [2] and thus they will not be described further here.

Dedicated to Professor Tim Clark on the occasion of his 60th birthday.

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## Parameterisation data

The target values used for parameterisation and their sources are defined in Tables S1, S2 and S3 in the electronic supplementary material (ESM). For the parameterisation of gold, we used heats of formation, Koopmans' ionisation potentials, dipole moments and geometrical variables, as we did for Ti and Zr [2], Cu and Zn [3], Br and I [4], V and Cr [5], Co and Ni [6], Mn and Fe [7] parameterisations. Parameterisation data were extended with a small series of compounds whose target values were derived from DFT calculations. As before [1–7], we also checked that experimental values for heats of formation were reasonable using DFT calculations.

DFT calculations used the Gaussian 03 suite of programs [18] with the LANL2DZ basis set and standard effective core potentials [19–22] augmented by a set of polarisation functions [23] (designated LANL2DZ+pol) and the B3LYP hybrid functional [24–26].

Experimental parameterisation data for gold were taken largely from the NIST Webbook [27], but also from the OpenMopac collection [28], and the other experimental and theoretical sources given in the ESM.

The energetic parameterisation data and their sources are given in Table S1. In addition to the energetic data, geometries, dipole moments and ionisation potentials taken from the above sources, crystal structures from the Cambridge Structural Database (CSD) [29] were used in the parameterisation to ensure that not only the energetic and electronic properties for the “prototype” compounds, but also the structures of large gold compounds are well produced.

## Results

The optimised AM1\* parameters are shown in Table 1. Geometries were optimised with the new AM1\* parameterisation using VAMP 10.0 [30], while the PM6 calculations used MOPAC2007 [31]. The two programs give essentially identical results for the Hamiltonians that are available in both.

### Heats of formation

The calculated heats of formation for our training set of gold compounds are shown in Table 2. The results have been compared with the only comparable method available—Stewart's PM6 [32].

AM1\* reproduces the heats of formation of the training set, which consists of 49 gold compounds used in parameterisation, better than PM6. AM1\* shows no significant systematic error trend with a mean signed error

**Table 1** AM1\* parameters for Au

Parameter	Au
$U_{ss}$ [eV]	−87.9070798
$U_{pp}$ [eV]	−105.2325082
$U_{dd}$ [eV]	−86.3002150
$\zeta_s$ [bohr <sup>−1</sup> ]	2.9612383
$\zeta_p$ [bohr <sup>−1</sup> ]	2.0921916
$\zeta_d$ [bohr <sup>−1</sup> ]	4.2954046
$\beta_s$ [eV]	−10.5044093
$\beta_p$ [eV]	−2.9212915
$\beta_d$ [eV]	−26.0306918
$g_{ss}$ [eV]	12.8779541
$g_{pp}$ [eV]	41.6610633
$g_{sp}$ [eV]	10.4094935
$g_{p2}$ [eV]	37.2533670
$h_{sp}$ [eV]	0.2611095
$z_{sn}$ [bohr <sup>−1</sup> ]	3.3536714
$z_{pn}$ [bohr <sup>−1</sup> ]	7.8813347
$z_{dn}$ [bohr <sup>−1</sup> ]	1.7991401
$\rho(\text{core})$ [bohr <sup>−1</sup> ]	1.3923445
$\Delta H_f^{\circ}(\text{atom})$ [kcal mol <sup>−1</sup> ]	88.0
$F_{sd}^0$ [eV]	7.7583836
$G_{sd}^2$ [eV]	6.0090661
$\alpha(\text{ij})$	
H	2.6891239
C	3.1012172
N	2.5099816
O	3.3201280
F	2.5990722
Al	1.9195605
Si	1.4489186
P	3.3822499
S	2.4757345
Cl	2.5963772
Ti	0.8968304
V	3.9464525
Cr	2.0645066
Mn	3.0829513
Fe	2.8842586
Co	2.4940667
Ni	3.9231603
Cu	2.2444292
Zn	4.3646875
Br	2.2685919
Zr	1.3454899
Mo	1.3740902
I	4.3466246
Au	2.7869271
$\delta(\text{ij})$	
H	−2.3071373
C	7.7686410

**Table 1** (continued)

Parameter	Au
N	2.0238749
O	8.1526001
F	2.0413648
Al	1.6916486
Si	0.2684171
P	22.0561933
S	2.0695945
Cl	3.0310645
Ti	0.2436297
V	195.3767955
Cr	1.7484764
Mn	10.1393842
Fe	7.0870550
Co	3.7260808
Ni	51.9934681
Cu	1.4743149
Zn	51.6768894
Br	1.2652966
Zr	0.5332656
Mo	0.6104390
I	178.8807263
Au	6.0750313

(MSE) of  $-0.7 \text{ kcal mol}^{-1}$ , whereas PM6 tends to overestimate heats of formation to gold compounds by  $7.5 \text{ kcal mol}^{-1}$ . The mean unsigned error (MUE) between experimental and AM1\*-calculated heats of formation is only  $11.4 \text{ kcal mol}^{-1}$  and the root mean square deviation (RMSD) is  $19.4 \text{ kcal mol}^{-1}$ . These values are smaller than those given by PM6 (MUE= $23.1 \text{ kcal mol}^{-1}$  and RMSD= $33.7 \text{ kcal mol}^{-1}$ ). PM6 produces large errors for the compounds that were not included in its original training set. For example, PM6 gives errors in heats of formation of more than  $50 \text{ kcal mol}^{-1}$  for the compounds AuAlH<sub>2</sub>, AuPH<sub>3</sub><sup>+</sup>, AuV, AuNi and AuCu. However, Table 2 also shows the performance of AM1\* and PM6 for only the PM6 parameterisation dataset, which consists of 32 gold-containing compounds [32]. The AM1\* MUE of only  $10.7 \text{ kcal mol}^{-1}$  and RMSD of  $15.6 \text{ kcal mol}^{-1}$  compared with  $12.8 \text{ kcal mol}^{-1}$  (MUE) and  $15.9 \text{ kcal mol}^{-1}$  (RMSD) for PM6 are very respectable and suggest that AM1\* is parameterised well and also performs better than PM6 for the PM6 parameterisation subset.

Large positive errors for AM1\* were found for Au(CH<sub>3</sub>)F<sub>2</sub> ( $47.0 \text{ kcal mol}^{-1}$ ), AuCl<sub>2</sub><sup>-</sup> ( $31.6 \text{ kcal mol}^{-1}$ ) and Au(CO)<sub>4</sub><sup>+</sup> ( $27.4 \text{ kcal mol}^{-1}$ ). The largest negative errors were found for AuZrH ( $-81.9 \text{ kcal mol}^{-1}$ ), AuPH<sub>3</sub><sup>+</sup> ( $-48.2 \text{ kcal mol}^{-1}$ ) and AuMo ( $-35.4 \text{ kcal mol}^{-1}$ ). The large errors with

Au(CH<sub>3</sub>)F<sub>2</sub> and Au(CO)<sub>4</sub><sup>+</sup> are not very surprising, since AM1\* uses the unchanged AM1 parameterisation for the elements H, C, N, O and F, and this limits the possible accuracy of the parameterisation. However, this does not explain the large error with AuCl<sub>2</sub><sup>-</sup>, AuZrH, AuPH<sub>3</sub><sup>+</sup> and AuMo. With the exception of the hydrogen in AuZrH and AuPH<sub>3</sub><sup>+</sup>, these compounds contain only pure AM1\* elements. As found for other metals, the large errors in these pure AM1\* element-containing compounds is likely to be a consequence of our sequential parameterisation strategy, in contrast to the simultaneous parameterisation used for PM6 [32].

#### Ionisation potentials and dipole moments

Table 3 shows a comparison of the calculated and experimental Koopmans' theorem ionisation potentials and dipole moments for AM1\* and PM6.

AM1\* performs marginally better than PM6 for the ionisation potentials with an MUE of  $0.38 \text{ eV}$ , compared with  $1.19 \text{ eV}$  for PM6. Here, one should note that all the experimental ionisation potential data were taken from the NIST Webbook [27] and that no details of the performance for ionisation potentials of gold compounds was given in the original PM6 parameterisation of gold [32]. On the other hand, only Au and Au<sub>2</sub> were used in the training set for AM1\* parameterisation and the remaining compounds were used for the test step. The largest AM1\* errors, i.e. more than  $0.5 \text{ eV}$ , are found for AuAl, AuAl<sub>2</sub> and Au<sub>2</sub>Al ( $0.63$ ,  $0.51$  and  $0.70 \text{ eV}$ , respectively). Both AM1\* and PM6 tend to give positive systematic errors for ionisation potentials of gold-containing compounds with MSEs of  $0.13$  and  $0.25 \text{ eV}$ , respectively.

The AM1\* training set for dipole moments consists of 14 compounds taken directly from the PM6 parameterisation dataset and was not extended. AM1\* underestimates the dipole moments of gold-containing compounds by  $-0.33$  Debye for this dataset, whereas PM6 tends to give positive systematic errors with an MSE of  $0.21$  Debye. The performance of the two methods is comparable for dipole moments. The mean unsigned errors are found to be  $0.77$  Debye and  $0.78$  Debye for AM1\* and PM6, respectively. AM1\* errors larger than  $1.0$  Debye, are found for the compounds Au(NH<sub>2</sub>)<sub>3</sub> ( $-2.06$  Debye), AuI ( $1.53$  Debye), Au(CH<sub>3</sub>)F<sub>2</sub> ( $-1.50$  Debye), AuF ( $1.19$  Debye), Au(CH<sub>3</sub>)<sub>3</sub> ( $-1.13$  Debye), Au(CH<sub>3</sub>)<sub>2</sub>(OH) ( $-1.10$  Debye). With the sole exception of AuI, these compounds contain the original AM1 elements H, C, N, O and F, which limits the possible accuracy of the parameterisation. The large error with AuI is also not very surprising as it is a result of the known weakness of AM1\* parameterisation for iodine in reproducing dipole moments [4].

**Table 2** Calculated AM1\* and PM6 heats of formation and errors compared with our target values for the gold-containing compounds used to parameterise AM1\* (all values kcal mol<sup>-1</sup>). Errors are classified by colouring the boxes in which they appear. *Green* Errors

lower than 10 kcal mol<sup>-1</sup>, *yellow* 10–20 kcal mol<sup>-1</sup>, *pink* errors greater than 20 kcal mol<sup>-1</sup>. The codenames within parentheses indicate the Cambridge Structural Database (CSD)-names of the compounds

Compound	Target	AM1*		PM6	
	$\Delta H_f^\circ$	$\Delta H_f^\circ$	Error	$\Delta H_f^\circ$	Error
Au	88.0	88.0	0.0	77.5	-10.5
Au <sup>-</sup>	20.0	8.3	-11.7	33.0	13.0
Au <sup>+</sup>	300.7	286.0	-14.7	286.6	-14.1
Au <sub>2</sub>	87.0	114.1	27.1	84.7	-2.3
AuH	78.7	82.5	3.8	67.5	-11.2
AuH <sub>3</sub>	149.1	128.7	-20.5	136.5	-12.6
AuCH <sub>3</sub>	67.3	73.1	5.8	77.4	10.1
Au(CH <sub>3</sub> ) <sub>3</sub>	84.7	88.1	3.4	61.8	-22.9
AuNH <sub>2</sub>	93.9	96.1	2.2	95.8	1.9
Au(CH <sub>3</sub> ) <sub>2</sub> (NH <sub>2</sub> )	83.9	98.8	14.9	99.7	15.8
Au(CN) <sub>2</sub> <sup>-</sup>	54.9	50.5	-4.5	65.5	10.6
Au(NH <sub>2</sub> ) <sub>3</sub>	126.0	121.9	-4.1	131.3	5.3
Au(NH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	154.5	174.1	19.6	166.6	12.1
Au(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	355.1	346.9	-8.2	367.0	11.9
(Au(CH <sub>3</sub> ) <sub>2</sub> (CN)) <sub>4</sub>	362.7	361.3	-1.4	364.2	1.5
AuO <sup>-</sup>	57.1	54.4	-2.7	46.0	-11.1
AuOH	57.8	46.0	-11.8	50.2	-7.6
Au(CH <sub>3</sub> ) <sub>2</sub> (OH)	45.7	45.2	-0.5	66.9	21.2
Au(H <sub>2</sub> O) <sub>4</sub> <sup>+</sup>	-37.8	-43.7	-5.9	9.7	47.5
Au(CO) <sub>4</sub> <sup>+</sup>	141.1	168.5	27.4	108.8	-32.3
AuF	50.0	55.4	5.4	83.6	33.6
AuF <sub>3</sub>	12.7	12.7	0.0	39.1	26.4
AuF <sub>4</sub> <sup>-</sup>	-79.7	-82.5	-2.8	-113.5	-33.8
Au(CH <sub>3</sub> )F <sub>2</sub>	-10.0	37.0	47.0	25.4	35.4
AuAlH <sub>2</sub>	90.6	90.5	-0.1	163.8	73.2
AuSiH <sub>3</sub>	84.1	84.1	0.0	125.1	41.0
AuPH <sub>3</sub> <sup>+</sup>	260.8	212.6	-48.2	192.6	-68.2
AuSH <sub>2</sub> <sup>+</sup>	269.1	246.6	-22.5	243.2	-25.9
AuF <sub>2</sub> (SH)	7.6	17.0	9.4	23.2	15.6
Au(Me <sub>2</sub> S) <sub>2</sub>	148.8	148.6	-0.2	154.6	5.8
AuCl	60.2	67.6	7.4	69.5	9.3
AuCl <sub>2</sub> <sup>-</sup>	-67.1	-35.5	31.6	-70.4	-3.3
AuCl <sub>3</sub>	65.1	51.4	-13.7	58.0	-7.1
AuCl <sub>4</sub> <sup>-</sup>	-89.7	-89.7	0.0	-92.9	-3.2
AuTi	145.7	145.7	0.0	111.2	-34.5
AuV	100.2	107.0	6.8	203.3	103.1
AuCr	137.0	136.1	-0.9	173.2	36.2
AuCo	141.5	141.6	0.1	132.4	-9.1
AuNi	77.8	77.8	0.0	178.8	101.0
AuCu	117.7	117.7	0.0	200.1	82.4
AuZnH	94.5	94.5	0.0	82.7	-11.8
AuBr	62.8	68.7	5.9	68.9	6.1
AuBr <sub>2</sub> <sup>-</sup>	-56.3	-50.9	5.4	-50.1	6.2
AuBr <sub>4</sub> <sup>-</sup>	-66.4	-71.5	-5.1	-70.0	-3.6
AuZrH	173.0	91.1	-81.9	166.7	-6.3
AuMo	251.5	216.1	-35.4	209.6	-41.9
AuI	69.0	92.5	23.5	79.0	10.0
AuI <sub>2</sub> <sup>-</sup>	-38.1	-22.5	15.6	-24.5	13.6
AuI <sub>4</sub> <sup>-</sup>	-26.8	-27.9	-1.1	-37.5	-10.7

	AM1*	PM6
<b>N=49</b>		
Most positive error	47.0	103.1
Most negative error	-81.9	-68.2
MSE	-0.7	7.5
MUE	11.4	23.1
RMSD	19.4	33.7

### Results for the PM6 parameterization set (N=32)

MSE	5.2	2.4
MUE	10.7	12.8
RMSD	15.6	15.9

**Table 3** Calculated AM1\* and PM6 Koopmans' theorem ionisation potentials and dipole moments for gold-containing compounds. The errors are colour coded as follows: *green* up to 0.5 eV or 0.5 Debye; *yellow* between 0.5 and 1.0; *pink* larger than 1.0

Compound	Target	AM1*		PM6	
Koopmans' Theorem Ionization Potentials for Cobalt Compounds (eV)					
		AM1*	Error	PM6	Error
Au	9.22	9.42	0.20	9.07	-0.15
Au <sub>2</sub>	8.70	8.69	-0.01	11.42	2.72
AuAl	7.60	8.23	0.63	8.01	0.41
AuAl <sub>2</sub>	6.20	6.71	0.51	5.79	-0.41
Au <sub>2</sub> Al	7.70	8.40	0.70	8.89	1.19
AuSi	9.50	9.17	-0.33	7.72	-1.78
Au(CH <sub>3</sub> )P(CH <sub>3</sub> ) <sub>3</sub>	7.70	7.26	-0.44	6.27	-1.43
Au(CH <sub>3</sub> ) <sub>3</sub> P(CH <sub>3</sub> ) <sub>3</sub>	7.80	7.55	-0.25	9.23	1.43
		AM1*		PM6	
<b>N=8</b>					
MSE		0.13		0.25	
MUE		0.38		1.19	
Dipole Moments for Cobalt Compounds (Debye)					
	Target	AM1*	Error	PM6	Error
AuH	0.95	1.16	0.21	0.08	-0.87
AuCH <sub>3</sub>	0.46	0.05	-0.41	0.38	-0.08
Au(CH <sub>3</sub> ) <sub>3</sub>	1.78	0.65	-1.13	0.41	-1.37
AuNH <sub>2</sub>	1.63	1.70	0.07	2.73	1.10
Au(CH <sub>3</sub> ) <sub>2</sub> (NH <sub>2</sub> )	0.34	0.42	0.08	1.19	0.85
Au(NH <sub>2</sub> ) <sub>3</sub>	3.02	0.96	-2.06	5.76	2.74
AuOH	2.53	3.31	0.78	2.62	0.09
Au(CH <sub>3</sub> ) <sub>2</sub> (OH)	3.74	2.64	-1.10	3.04	-0.70
AuF	4.04	2.85	-1.19	5.47	1.43
Au(CH <sub>3</sub> )F <sub>2</sub>	2.46	0.96	-1.50	2.85	0.39
AuF <sub>2</sub> (SH)	1.60	1.32	-0.28	1.93	0.33
AuCl	3.48	3.86	0.38	3.35	-0.13
AuBr	2.87	2.89	0.02	2.11	-0.76
AuI	2.21	3.74	1.53	2.11	-0.10
		AM1*		PM6	
<b>N=14</b>					
MSE		-0.33		0.21	
MUE		0.77		0.78	

**Table 4** Calculated AM1\* and PM6 bond lengths and angles for gold-containing compounds. The codenames within parentheses indicate the CSD-names of the compounds. The errors are colour

coded as follows: *green* up to 0.05 Å or 0.5°; *yellow* between 0.05–0.1 Å or 0.5–1.0°; *pink* larger than 0.1 Å or 1°

Compound	Variable	Target	AM1*		PM6	
				Error		Error
Au <sub>2</sub>	Au-Au	2.63	2.63	0.00	2.24	-0.39
Au <sub>2</sub> <sup>-</sup>	Au-Au	2.73	2.67	-0.07	2.49	-0.24
AuH	Au-H	1.52	1.52	0.00	1.53	0.01
AuH <sub>3</sub>	Au-H	1.70	1.58	-0.13	1.71	0.01
	H-Au-H	120.0	119.4	-0.6	120.0	0.0
AuCH <sub>3</sub>	Au-C	2.08	2.11	0.03	2.07	-0.01
	H-C-Au	107.2	107.3	0.1	107.1	-0.1
Au(CH <sub>3</sub> ) <sub>3</sub>	Au-C	2.06	2.10	0.04	2.00	-0.06
	Au-C'	2.12	2.11	-0.01	2.02	-0.11
	C-Au-C	176.1	160.1	-16.0	169.4	-6.7
AuNH <sub>2</sub>	Au-N	2.09	2.00	-0.09	1.53	-0.56
Au(CH <sub>3</sub> ) <sub>2</sub> (NH <sub>2</sub> )	Au-C	2.13	2.10	-0.03	2.06	-0.07
	C-Au-C	80.1	86.5	6.4	105.3	25.2
	Au-N	2.04	1.99	-0.05	1.60	-0.44
Au(CN) <sub>2</sub> <sup>-</sup>	Au-C	2.04	2.08	0.04	2.09	0.05
	C-Au-C	180.0	180.0	0.0	180.0	0.0
Au(CN) <sub>2</sub> <sup>-</sup> (JEYXAM)	Au-C	2.02	2.05	0.03	2.09	0.07
	C-N	1.11	1.16	0.05	1.15	0.04
AuC <sub>3</sub> N <sub>2</sub> H <sub>3</sub> (CYMIAU)	Au-C(N)	2.00	2.13	0.13	2.05	0.05
	Au-C(NCH <sub>3</sub> )	1.98	2.05	0.07	2.15	0.17
Au(NH <sub>2</sub> ) <sub>3</sub>	Au-N	2.08	1.99	-0.09	1.42	-0.66
	N-Au-N	158.1	156.0	-2.1	139.3	-18.9
	Au-N'	2.11	2.05	-0.06	2.03	-0.08
Au(NH <sub>3</sub> ) <sub>4</sub> <sup>3+</sup>	Au-N	2.17	2.17	0.00	2.14	-0.03
Au(NH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	Au-N	2.50	2.56	0.06	2.35	-0.15
AuC <sub>14</sub> N <sub>4</sub> H <sub>22</sub> <sup>+</sup> (AZEGIV)	Au-N	1.99	2.03	0.04	2.14	0.15
	Au-N'	1.97	2.03	0.06	2.02	0.05
	N-Au-N	95.6	94.7	-0.9	86.2	-9.4
Au(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	Au-N	2.67	2.47	-0.20	2.47	-0.20
	Au-N'	2.24	2.45	0.21	2.61	0.37
Au <sub>2</sub> C <sub>6</sub> N <sub>2</sub> H <sub>2</sub> O (DEVLUL)	Au-N	2.14	2.21	0.07	2.18	0.04
	Au-C	2.04	2.10	0.06	2.00	-0.04
	C-Au-N	97.1	93.2	-3.9	95.2	-1.9
(Au(CH <sub>3</sub> ) <sub>2</sub> (CN)) <sub>4</sub>	Au-Au	5.50	5.53	0.03	5.53	0.03
	Au-C(CN)	2.03	2.10	0.07	2.11	0.08
	Au-N	2.14	2.22	0.08	2.28	0.14
	Au-C(Me)	2.11	2.15	0.04	1.98	-0.13
AuO <sup>-</sup>	Au-O	1.98	1.98	0.00	1.43	-0.55
AuOH	Au-O	1.98	2.08	0.10	1.42	-0.56
Au(CH <sub>3</sub> ) <sub>2</sub> (OH)	Au-O	2.09	2.10	0.01	1.88	-0.21
	Au-C	2.10	2.10	0.00	2.00	-0.10
	O-Au-C	106.0	135.1	29.1	98.2	-7.8
Au(H <sub>2</sub> O) <sub>2</sub> <sup>+</sup>	O-Au-O	176.8	172.1	-4.7	176.9	0.1
Au(H <sub>2</sub> O) <sub>4</sub> <sup>+</sup>	Au-O	2.46	2.46	0.00	2.39	-0.07
	Au-O'	2.45	2.45	0.00	2.36	-0.09
Au(CO) <sub>4</sub> <sup>+</sup>	Au-C	2.28	2.34	0.06	2.30	0.02
AuF	Au-F	2.07	1.95	-0.12	1.92	-0.15
Au(CH <sub>3</sub> )F <sub>2</sub>	Au-F	1.96	1.98	0.02	2.06	0.11
	Au-C	2.05	2.04	-0.01	1.94	-0.11



	C-Au-F	91.6	99.7	8.1	96.7	5.1
AuF <sub>3</sub>	Au-F	2.01	2.04	0.03	2.04	0.03
	Au-F'	2.02	1.98	-0.04	1.94	-0.08
	F-Au-F'	95.0	99.2	4.2	102.5	7.5
AuF <sub>4</sub> <sup>-</sup>	Au-F	1.97	2.00	0.03	2.03	0.07
AuAlH <sub>2</sub>	Au-Al	2.38	2.42	0.03	3.01	0.63
AuSiH <sub>3</sub>	Au-Si	2.32	2.32	0.00	3.38	1.06
AuPH <sub>3</sub> <sup>+</sup>	Au-P	2.28	2.39	0.11	2.11	-0.17
AuPH <sub>2</sub>	Au-P	2.33	2.28	-0.05	2.09	-0.24
AuP <sup>2-</sup>	Au≡P	2.28	2.20	-0.08	1.59	-0.69
Au(PH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Au-P	2.38	2.34	-0.04	2.20	-0.18
Au <sub>2</sub> C <sub>10</sub> P <sub>4</sub> H <sub>28</sub> <sup>+</sup> (DUKREG01)	Au-P	2.30	2.39	0.09	2.39	0.09
	P-Au-P	176.8	177.0	0.3	91.0	-85.8
AuSH	Au-S	2.30	2.29	-0.01	2.18	-0.12
AuSH <sub>2</sub> <sup>+</sup>	Au-S	2.37	2.48	0.12	2.13	-0.24
Au <sub>2</sub> C <sub>8</sub> H <sub>22</sub> S <sub>2</sub> (CULYIR)	Au-Au	3.46	3.59	0.13	3.51	0.05
	Au-S	2.41	2.42	0.01	2.32	-0.09
	Au-C	2.13	2.11	-0.02	2.00	-0.13
	C-Au-Au	134.8	131.2	-3.6	132.8	-1.9
AuF <sub>2</sub> (SH)	Au-S	2.34	2.26	-0.08	2.16	-0.18
	Au-F	2.02	1.99	-0.03	2.04	0.02
	S-Au-F	89.4	97.3	7.9	87.0	-2.3
AuC <sub>2</sub> N <sub>4</sub> H <sub>8</sub> S <sub>2</sub> <sup>+</sup> (AFAWUZ)	Au-S	2.28	2.25	-0.03	2.28	0.00
AuC <sub>12</sub> H <sub>8</sub> S <sub>4</sub> (JEKGAH)	Au-S	2.30	2.27	-0.03	2.25	-0.05
	S-Au-S	89.9	92.7	2.9	92.9	3.0
Au(Me <sub>2</sub> S) <sub>2</sub> <sup>+</sup>	Au-S	2.40	2.36	-0.04	2.30	-0.10
AuCl	Au-Cl	2.33	2.26	-0.07	2.34	0.01
AuCl <sub>2</sub> <sup>-</sup> (GANJOU)	Au-Cl	2.28	2.28	0.00	2.42	0.14
AuCl <sub>3</sub>	Au-Cl	2.32	2.22	-0.10	2.20	-0.12
	Au-Cl	2.30	2.23	-0.07	2.06	-0.25
AuCl <sub>4</sub> <sup>-</sup> (BENYAU)	Au-Cl	2.27	2.25	-0.02	2.27	0.00
AuC <sub>4</sub> N <sub>3</sub> H <sub>13</sub> Cl <sup>2+</sup> (AEMAUP)	Au-Cl	2.27	2.20	-0.07	2.13	-0.14
	Au-N	1.97	2.20	0.23	2.21	0.24
	N-Au-Cl	93.7	99.1	5.4	90.5	-3.2
	Au-N'	2.05	2.26	0.21	2.06	0.01
AuC <sub>2</sub> H <sub>6</sub> SCI (GOJLAS)	Au-S	2.27	2.35	0.08	2.33	0.06
	Au-Cl	2.29	2.25	-0.04	2.38	0.09
Au(CH <sub>3</sub> )Cl <sub>2</sub>	Au-Cl	2.35	2.23	-0.12	2.31	-0.04
	C-Au-Cl	93.0	93.6	0.6	93.8	0.8
	Cl-Au-Cl	177.9	175.7	-2.2	177.9	0.0
AuC <sub>11</sub> N <sub>2</sub> H <sub>10</sub> Cl <sub>2</sub> O <sub>2</sub> <sup>+</sup> (BATTOF)	Au-Cl	2.26	2.31	0.05	2.16	-0.10
	Cl-Au-Cl	89.6	138.6	49.0	99.3	9.7
	Au-N	2.08	2.36	0.28	2.19	0.11
AuC <sub>6</sub> NH <sub>3</sub> Cl <sub>2</sub> O <sub>3</sub> (KUDNAY)	Au-Cl	2.25	2.23	-0.02	2.41	0.16
	Au-N	2.04	2.04	0.00	2.35	0.31
	Au-O	1.99	2.07	0.08	1.42	-0.57
AuC <sub>5</sub> NH <sub>5</sub> Cl <sub>3</sub> (PYAUCL10)	Au-Cl	2.29	2.25	-0.04	2.28	-0.01
	Au-Cl	2.26	2.22	-0.04	2.16	-0.10
	Au-Cl	2.28	2.24	-0.04	2.27	-0.01
	Au-N	2.00	2.25	0.25	2.17	0.17
AuC <sub>6</sub> NH <sub>7</sub> Cl <sub>3</sub> O (HIHCIK)	Au-Cl	2.27	2.31	0.04	2.26	-0.01

Au <sub>2</sub> C <sub>12</sub> P <sub>2</sub> H <sub>28</sub> Cl <sub>2</sub> (EMPLAU)	Au-N	2.02	2.07	0.05	2.13	0.11
	Au-Cl	2.38	2.32	-0.06	2.45	0.07
	Au-C	2.05	2.17	0.12	2.23	0.18
	Cl-Au-C	85.8	88.4	2.7	93.1	7.3
	Au-Au	2.59	2.65	0.06	3.13	0.54
AuTi	Au-Ti	2.52	2.52	0.00	3.60	1.07
AuV	Au-V	2.53	2.53	0.00	3.60	1.07
AuCr	Au-Cr	2.54	2.54	0.00	5.54	3.00
AuCo	Au-Co	2.44	2.43	0.00	3.51	1.08
AuNi	Au-Ni	2.41	2.40	-0.01	6.34	3.93
AuCu	Au-Cu	2.39	2.40	0.00	3.78	1.39
AuZn	Au-Zn	2.50	2.58	0.08	2.80	0.30
AuZnH	Au-Zn	2.42	2.36	-0.06	2.80	0.38
AuBr	Au-Br	2.44	2.30	-0.15	2.26	-0.18
AuBr <sub>2</sub> <sup>-</sup> (DOYMAF)	Au-Br	2.38	2.33	-0.05	2.43	0.05
AuBr <sub>4</sub> <sup>-</sup>	Au-Br	2.55	2.35	-0.20	2.28	-0.27
AuC <sub>2</sub> H <sub>6</sub> SBr (GIGWAU)	Au-Br	2.40	2.30	-0.10	2.34	-0.06
AuC <sub>3</sub> PH <sub>9</sub> Br <sub>3</sub> (BRMPAU)	Au-S	2.28	2.35	0.07	2.32	0.04
	Au-Br	2.51	2.82	0.31	2.49	-0.02
	Au-Br'	2.48	2.29	-0.19	2.97	0.49
	Au-P	2.48	2.54	0.06	2.08	-0.40
AuC <sub>2</sub> H <sub>6</sub> SBr <sub>3</sub> (GIGWEY)	Au-Br	2.42	2.42	0.00	2.84	0.42
	Au-S	2.35	2.32	-0.03	2.39	0.04
AuZrH	Au-Zr	2.70	2.70	0.00	3.19	0.49
AuMo	Au-Mo	2.62	2.62	0.00	3.70	1.08
AuI	Au-I	2.61	2.80	0.19	2.57	-0.04
AuI <sub>2</sub> <sup>-</sup> (GANJUA)	Au-I	2.53	2.54	0.01	2.67	0.14
AuI <sub>4</sub> <sup>-</sup> (GEJQUH)	Au-I	2.63	2.55	-0.08	2.91	0.28
Au <sub>2</sub> C <sub>9</sub> P <sub>2</sub> H <sub>23</sub> I (BIBPIL)	Au-Au	2.70	3.16	0.46	3.22	0.52
	Au-I	2.89	2.53	-0.36	2.67	-0.22
	Au-C	2.13	2.12	-0.01	2.11	-0.02
	Au-C(P)	2.09	2.17	0.08	2.11	0.02
	C-Au-Au	88.8	87.3	-1.5	121.3	32.5
	Au-I	2.58	2.53	-0.06	2.65	0.07
Au <sub>2</sub> C <sub>6</sub> P <sub>2</sub> H <sub>18</sub> I <sub>2</sub> (FUWFIM)	Au-P	2.26	2.39	0.13	2.32	0.06
				<b>AM1*</b>	<b>PM6</b>	
<b>N=113</b>						
<b>MSE bond length</b>				0.01	0.10	
<b>MUE bond length</b>				0.07	0.28	
<b>N=22</b>						
<b>MSE bond angle</b>				3.7	-2.1	
<b>MUE bond angle</b>				6.9	10.4	

## Geometries

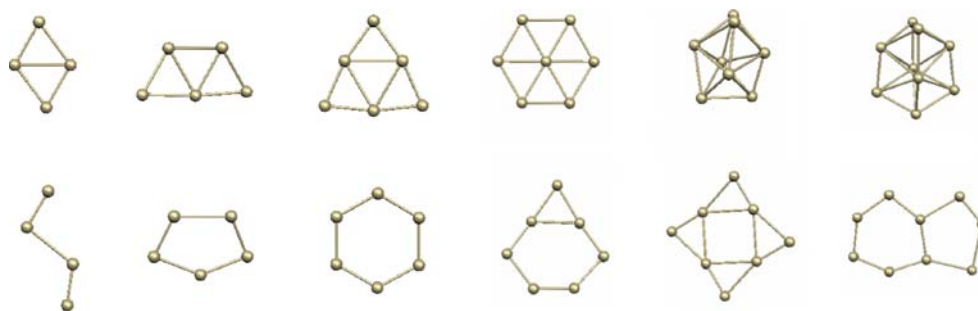
The geometrical parameters used to parameterise AM1\* for gold, and a comparison and statistical analysis of the AM1\* and PM6 results are shown in Table 4.

AM1\* shows no significant systematic error for gold, with an MSE of 0.01 Å. In contrast to AM1\*, PM6, with an MSE of 0.10 Å, predicts the bond lengths of the gold-containing compounds to be too long. AM1\*, with an MUE of 0.07 Å, performs far better than PM6 (MUE=

0.28 Å) for the training set, which consists of 75 compounds. Once again, as in heats of formation, large errors for PM6 originate from compounds not included in the original PM6 parameterisation dataset. In the case of bond angles, AM1\* performs quite well (MUE=6.9°) compared to PM6 (MUE=10.4°). AM1\* overestimates bond angles at gold systematically with an MSE of 3.7°, whereas PM6 underestimates them by -2.1°. However, AM1\* not only performs well for its own extended dataset, it also performs better for the PM6 parameterisation subset,



**Fig. 1** AM1\* (upper row) and PM6 (lower row) optimised structures of neutral gold clusters with four to nine atoms



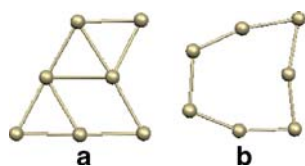
which consists of 50 compounds [32]. For the PM6 training set, AM1\* gives MUEs of 0.08 Å for bond lengths and 7.5° for bond angles, whereas PM6 gives MUEs of 0.15 Å and 12.4° for bond lengths and angles, respectively.

The AM1\* and PM6 optimised ground state structures of neutral gold clusters with four to nine atoms are shown in Fig. 1. PM6 predicts neutral gold clusters up to nine atoms to be planar as reported earlier by Stewart. [32] AM1\* gives planar structures up to seven atoms. AM1\* finds non-planar 3D structures for gold clusters with more than eight atoms, in good agreement with Häkkinen and Landman's results obtained from DFT with scalar-relativistic ab initio pseudopotentials and a generalised gradient correction. [33] On the other hand, Gruene et al. [34] proposed a planar edge-capped triangle with  $C_s$  symmetry to be lowest in energy for neutral  $Au_7$  on the strength of experimental vibrational spectra and DFT calculations within the generalised gradient approximation, in contrast to Häkkinen and Landman's hexagonal planar structure [33] and the 3D pentagonal bipyramidal structure from DFT with local density approximation of Wang et al. [35].

As shown in Fig. 2, AM1\* reproduces the planar edge-capped triangle  $Au_7$  structure very well, but finds it to be 7.38 kcal mol<sup>-1</sup> higher in energy than the hexagonal structure. PM6 does not reproduce the structure of this isomer structure well, but finds it to be 0.23 kcal mol<sup>-1</sup> lower in energy than the hexagonal structure.

Very recently, Botana et al. [36] performed an LCGTO-KSDFM DFT [37] study and found that the global energy minimum for  $Au_8$  is a planar  $D_{4h}$  tetra-capped square structure. A non-planar  $D_{2d}$  bi-capped octahedron structure was found to be the second lowest energy structure. Wang et al. [35] proposed a  $T_d$  bicapped octahedron structure using relativistic effective core potentials (ECP) and a double numerical basis with  $d$ -polarisation functions. Their results are consistent with Häkkinen and Landman's

**Fig. 2** AM1\* (a) and PM6 (b) optimised structure of planar edge-capped triangle  $Au_7$  with  $C_s$  symmetry



generalised gradient approximation (GGA) results [33]. On the other hand, Olson and Gordon [38] found that a non-planar  $D_{2d}$  bi-capped octahedron structure is the lowest energy neutral  $Au_8$  isomer, using Møller-Plesset perturbation theory (MP2) [39] regardless of basis set or contributions from core-valence correlation. They also found that CCSD [40] calculations (with some exceptions due to core-valence correlation effects) give tetra-capped square structure as the minimum energy structure.

Since many different proposals originate from different level calculations, both AM1\* and PM6 perform reasonably well as far as we can tell.

## Discussion

The new AM1\* parameterisation for gold, for which the parameterisation dataset has been extended by including results from DFT calculations to produce a parameter set that is more robust and more reliable, provides an important additional element, especially for catalytic chemistry and biochemistry applications. AM1\* parameterisation for gold gives very good results for energetic, electronic and structural properties. AM1\* performs very well for its own training set and also for the PM6 parameterisation subset. In addition, for small neutral gold clusters, AM1\* performs very well especially regarding structural properties. Naturally, as with all semiempirical methods, there may be some cases for which both AM1\* and PM6 might show large deviations from experimental values. As published NDDO-based methods including  $d$ -orbitals, both AM1\* and PM6 provide the opportunity to perform comparative calculations for different applications and are good starting points for reaction specific local parameterisations.

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