Supplementary Material

Scalable Properties of Metal Clusters: A Comparative Study of Modern Exchange-Correlation Functionals

Ralph Koitz[1], Thomas M. Soini[1], Alexander Genest[1], S. B. Trickey[2], and Notker Rösch[1,3] *

[1] Department Chemie and Catalysis Research Center, Technische Universität München, 85748 Garching, Germany

[2] Quantum Theory Project, Dept. of Physics and Dept. of Chemistry, University of Florida, Gainesville, FL 32611, USA

[3] Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore

* Electronic mail: roesch@mytum.de

Further computational details

We used all-electron Gaussian-type basis sets: (18s13p9d) → [7s6p4d] for palladium[1] and (21s7p11d7f) → [8s7p5d3f] for gold.[2] Atomic eigenvectors were employed to construct general contractions. In PARAGAUSS, for the calculation of the Hartree potential, the electronic density is approximately represented by a set of fitting functions.[3, 4] The *s*- and r^2 exponents of this set of fitting functions were determined from a subset of the *s*-and *p*-orbital exponents scaled by a factor of 2; the fit basis was augmented by sets of five *p*- and *d*-type "polarization" exponents,[3] chosen as geometric series with factors of 2.5, starting at 0.1 and 0.2 au, respectively. The numerical integration grid for evaluating the various xc contributions was constructed as a superposition of atom-centered grids of Lebedev-type. These atomic grids were chosen to have 71 radial shells of 171 angular points. After grid pruning, the result is a symmetry-reduced grid size of about 24,000 points for Pd_{55}.

References

1. S. Huzinaga, J. Chem. Phys. **66**, 4245-4245 (1977).
2. O. D. Häberlen, S. C. Chung and N. Rösch, Int. J. Quantum Chem. **28**, 595-610 (1994).
3. B. I. Dunlap, N. Rösch and S. B. Trickey, Mol. Phys. **108**, 3167-3180 (2010).
4. B. I. Dunlap and N. Rösch, Adv. Quantum Chem. **21**, 317-339 (1990).

Table S1: Average bond lengths d_{av} in Pd_n clusters, optimized with 9 xc functionals, and parameters of linear fit as a function of $n^{-1/3}$ from scalar relativistic calculations. Distances in pm.

	VWN	BP	PW91	PBE	PBEsol	VMT	VMTsol	VT{84}	VT{84}sol
Pd_{13}	262.5	270.2	270.1	270.4	265.6	271.5	265.3	271.5	266.0
Pd_{19}	264.2	271.6	271.4	271.6	267.0	272.6	266.6	272.7	266.7
Pd_{38}	265.8	273.2	273.1	273.3	268.6	274.3	268.2	274.4	268.3
Pd_{55}	266.2	273.7	273.6	273.8	269.1	274.8	268.6	274.9	268.7
Pd_{79}	267.4	274.9	274.8	275.0	270.3	275.9	269.8	276.0	269.8
Pd_{147}	267.9	275.4	275.3	275.4	270.7	276.4	270.2	276.5	270.2
$r^{2\,a}$	0.982	0.990	0.989	0.990	0.987	0.990	0.988	0.990	0.984
$k^{\,b}$	-22.77	-22.45	-22.26	-21.81	-21.87	-21.37	-20.97	-21.33	-18.87
$d_{ext}{}^{\,d}$	272.5	279.9	279.7	279.7	275.1	280.6	274.4	280.7	273.9

[a] Squared correlation coefficient of linear fit; [b] slope in pm; [c] axis intercept in pm; [d] extrapolated bulk Pd-Pd distance

Table S2: Average bond lengths d_{av} in Pd_n clusters, optimized with 9 xc functionals, and parameters of linear fit as a function of $n^{-1/3}$ from nonrelativistic calculations. Distances in pm.

	VWN	BP	PW91	PBE	PBEsol	VMT	VMTsol	VT{84}	VT{84}sol
Pd_{13}	268.2	277.1	277.0	277.5	271.9	278.9	271.9	279.0	271.9
Pd_{19}	268.6	277.1	277.1	277.5	272.1	278.8	271.9	278.9	271.9
Pd_{38}	270.6	279.3	279.3	279.7	274.1	281.0	273.8	281.1	273.9
Pd_{55}	270.9	279.5	279.5	279.8	274.4	281.1	274.1	281.2	274.1
Pd_{79}	272.1	280.6	280.5	280.8	275.5	282.1	275.1	282.2	275.2
Pd_{147}	272.4	280.8	280.7	281.1	275.7	282.3	275.3	282.4	275.4
$r^{2\,a}$	0.974	0.951	0.950	0.943	0.958	0.932	0.949	0.931	0.949
$k^{\,b}$	-19.14	-18.08	-17.93	-17.32	-17.78	-16.66	-16.67	-16.60	-16.65
$d_{ext}{}^{\,d}$	276.2	284.5	284.3	284.5	279.2	285.6	278.7	285.7	-278.7

[a] Squared correlation coefficient of linear fit; [b] slope in pm; [c] axis intercept in pm; [d] extrapolated bulk Pd-Pd distance

Table S3: Average bond lengths d_{av} in Au_n clusters, optimized with 9 xc functionals, and parameters of linear fit as a function of $n^{-1/3}$. Distances in pm.

	VWN	BP	PW91	PBE	PBEsol	VMT	VMTsol	VT{84}	VT{84}sol
Au_{13}	273.7	282.2	281.9	282.0	283.0	283.2	276.2	283.2	276.2
Au_{19}	275.0	283.5	283.1	283.1	283.4	284.2	277.1	284.3	277.1
Au_{38}	277.5	286.0	285.6	285.5	285.9	286.6	279.5	286.7	279.5
Au_{55}	278.3	286.7	286.3	286.3	286.8	287.3	280.3	287.4	280.3
Au_{79}	279.4	288.0	287.3	287.4	287.6	288.4	281.3	288.5	281.3
$r^{2\,a}$	0.997	0.996	0.996	0.996	0.996	0.995	0.993	0.995	0.993
$k^{\,b}$	-29.56	-29.55	-28.03	-28.05	-28.18	-27.51	-26.91	-27.46	-26.89
$d_{ext}{}^{\,d}$	286.2	294.7	293.9	293.8	288.6	294.7	287.5	294.8	287.5

[a] Squared correlation coefficient of linear fit; [b] slope in pm; [c] axis intercept in pm; [d] extrapolated bulk Au-Au distance

Table S4: Cohesive energies E_{coh} of Pd_n clusters, optimized with 9 xc functionals, and parameters of linear fit as a function of $n^{-1/3}$ from scalar relativistic calculations. Energies in kJ·mol^{-1}

	VWN	BP	PW91	PBE	PBEsol	VMT	VMTsol	VT{84}	VT{84}sol
Pd_{13}	293.0	210.7	219.1	215.5	254.5	202.0	249.0	200.9	248.5
Pd_{19}	330.8	240.6	249.3	245.4	288.8	230.6	283.3	229.4	282.8
Pd_{38}	366.2	263.6	273.6	269.1	319.6	253.0	314.5	251.7	313.9
Pd_{55}	378.8	273.4	283.2	279.9	331.2	262.7	326.2	261.4	325.5
Pd_{79}	394.8	283.9	294.7	290.7	344.9	273.4	340.6	272.0	340.0
Pd_{147}	412.8	297.3	308.7	304.7	361.8	286.8	357.3	285.3	356.6
$r^{2\,a}$	0.989	0.983	0.985	0.986	0.989	0.986	0.989	0.985	0.9892
$k^{\,b}$	-493.8	-351.7	-364.4	-363.5	-440.1	-344.8	-444.9	-343.2	-444.1
$E_{bulk}{}^{c}$	509.5	366.1	379.7	375.6	447.6	353.9	444.0	352.1	443.2

[a] Squared correlation coefficient of linear fit; [b] slope in kJ·mol^{-1}; [c] extrapolated bulk cohesive energy in kJ·mol^{-1}

Table S5: Cohesive energies E_{coh} of Pd_n clusters, optimized with 9 xc functionals, and parameters of linear fit as a function of $n^{-1/3}$ from nonrelativistic calculations. Energies in kJ·mol^{-1}

	VWN	BP	PW91	PBE	PBEsol	VMT	VMTsol	VT{84}	VT{84}sol
Pd_{13}	293.0	210.7	219.1	215.5	254.5	202.0	249.0	200.9	248.5
Pd_{19}	330.8	240.6	249.3	245.4	288.8	230.6	283.3	229.4	282.8
Pd_{38}	366.2	263.6	273.6	269.1	319.6	253.0	314.5	251.7	313.9
Pd_{55}	378.8	273.4	283.2	279.9	331.2	262.7	326.2	261.4	325.5
Pd_{79}	394.8	283.9	294.7	290.7	344.9	273.4	340.6	272.0	340.0
Pd_{147}	412.8	297.3	308.7	304.7	361.8	286.8	357.3	285.3	356.6
$r^{2\,a}$	0.989	0.983	0.985	0.986	0.989	0.986	0.989	0.985	0.9892
$k^{\,b}$	-493.8	-351.7	-364.4	-363.5	-440.1	-344.8	-444.9	-343.2	-444.1
$E_{bulk}{}^{c}$	509.5	366.1	379.7	375.6	447.6	353.9	444.0	352.1	443.2

[a] Squared correlation coefficient of linear fit; [b] slope in kJ·mol^{-1}; [c] extrapolated bulk cohesive energy in kJ·mol^{-1}

Table S6: Cohesive energies E_{coh} of Au_n clusters, optimized with 9 xc functionals, and parameters of linear fit as a function of $n^{-1/3}$ from nonrelativistic calculations. Energies in kJ·mol^{-1}

	VWN	BP	PW91	PBE	PBEsol	VMT	VMTsol	VT{84}	VT{84}sol
Au_{13}	270.3	184.8	195.2	192.6	230.8	179.3	225.8	178.2	225.3
Au_{19}	300.7	206.3	217.6	214.7	257.7	200.0	252.9	198.8	252.3
Au_{38}	331.8	226.3	239.1	236.3	285.0	219.9	280.8	218.6	280.1
Au_{55}	343.7	235.9	249.0	246.1	296.2	229.3	292.1	227.9	291.4
Au_{79}	357.8	244.6	258.4	255.4	308.3	237.9	304.6	236.4	303.9
$r^{2\,a}$	0.992	0.991	0.992	0.992	0.993	0.992	0.993	0.992	0.993
$k^{\,b}$	-440.4	-301.1	-318.5	-317.0	-391.0	-295.5	-397.2	-293.7	-396.4
$E_{bulk}{}^{c}$	461.2	315.6	333.6	330.1	400.2	307.5	397.8	305.6	-397.0

[a] Squared correlation coefficient of linear fit; [b] slope in kJ·mol^{-1}; [c] extrapolated bulk cohesive energy in kJ·mol^{-1}

Table S7: Ionization potentials *IP*, electron affinities *EA*, and differences *IP–EA* data of Pd_n clusters, optimized with 9 xc functionals, and parameters of the linear fit as a function of $n^{-1/3}$. Energies in eV.

	VWN	BP	PW91	PBE	PBEsol	VMT	VMTsol	VT{84}	VT{84}sol
Pd_{13} [a]	6.72	6.47	6.40	6.33	6.40	6.27	6.23	6.27	6.23
Pd_{19} [a]	6.39	6.28	6.20	6.15	6.17	6.11	6.02	6.10	6.02
Pd_{38} [a]	6.56	6.24	6.18	6.10	6.23	6.04	6.07	6.03	6.07
Pd_{55} [a]	6.15	5.94	5.87	5.80	5.88	5.73	5.72	5.73	5.71
Pd_{79} [a]	6.18	5.95	5.88	5.81	5.89	5.75	5.74	5.74	5.73
Pd_{147} [a]	5.94	5.69	5.62	5.55	5.65	5.49	5.49	5.49	5.49
r^2 [b]	0.776	0.909	0.901	0.918	0.850	0.926	0.854	0.927	0.854
k [c]	2.87	3.04	3.06	3.06	2.88	3.14	2.87	3.15	2.88
Φ_{IP} [d]	5.47	5.19	5.12	5.05	5.18	4.95	5.02	4.96	5.02
Pd_{13} [e]	3.23	2.92	2.86	2.79	2.88	2.73	2.71	2.72	2.71
Pd_{19} [e]	3.09	3.04	2.96	2.90	2.89	2.87	2.73	2.87	2.72
Pd_{38} [e]	3.77	3.69	3.62	3.56	3.58	3.48	3.42	3.48	3.42
Pd_{55} [e]	3.79	3.66	3.58	3.52	3.55	3.46	3.38	3.46	3.38
Pd_{79} [e]	4.08	3.91	3.83	3.77	3.82	3.72	3.66	3.71	3.66
Pd_{147} [e]	4.25	4.03	3.95	3.89	3.96	3.83	3.83	3.83	3.80
r^2 [f]	0.909	0.959	0.954	0.956	0.940	0.966	0.946	0.966	0.943
k [g]	-4.93	-5.06	-5.02	-5.00	-5.05	-4.98	-5.16	-4.98	-5.09
Φ_{EA} [h]	5.17	5.04	4.96	4.89	4.95	4.83	4.82	4.82	4.79
r^2 [i]	0.977	0.998	0.996	0.997	0.991	0.998	0.990	0.998	0.991
k [j]	7.80	8.10	7.97	8.06	7.93	8.12	8.04	8.13	7.97
$\Delta\Phi$ [k]	0.30	0.15	0.16	0.16	0.23	0.13	0.20	0.13	0.23

[a] Ionization potential *IP*; [b] squared correlation coefficient of linear fits of *IP* data; [c] Slope of linear fit of *IP* data in eV; [d] Estimate of work function from *IP* values in eV; [e] Electron affinity *EA* in eV; [f] squared correlation coefficient of linear fit of *IP* data; [g] Slope of linear fit of *EA* data in eV; [h] Estimate of work function from *EA* values in eV; [i] squared correlation coefficient of linear fit of differences *IP–EA*; [j] Slope of linear fit of differences *IP–EA* in eV; [h] Difference Φ_{IP}–Φ_{EA} extrapolated from differences *IP–EA* in eV.