Supporting Information for

On the ground state of Pd$_{13}$

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1. Validation of Methodology

We first study the influence of the choice of functional on the atomic states of the Pd atom. For this purpose we employ the local density approximation (LDA) with Dirac exchange[1] and VWN correlation[2] (VWN), the generalized gradient approximation (GGA) in form of the PBE functional[3] and the meta-GGA level of approximation in form of the TPSS functional[4]. All calculations are performed with the 18 valence electron quasi-relativistic effective core potential (QECP18) and the corresponding basis set proposed by Andrae et al.[5] The GEN-A2* auxiliary function[6] set is used. In order to avoid spin contamination the restricted open-shell Kohn-Sham (ROKS) method is employed. The ^{3}D state is represented by the following one-determinant open-shell configuration:

$$(4d_{z^2})^1 \ (4d_{x^2-y^2})^2 \ (4d_{xy})^2 \ (4d_{xz})^2 \ (4d_{yz})^2 \ (5s)^1$$

The energy separations between the ^{1}S Pd ground state and the ^{3}D first excited state are given in Table 1 in wavenumbers. As this table shows the state ordering is correct at all levels of approximation.

Table 1: Energies for the ^{1}S $\rightarrow$ ^{3}D excitation in the Pd atom calculated at LDA, GGA and meta-GGA level of theory.

	E[cm^{-1}]				
State	VWN	PBE	TPSS	Exp[a]	Configuration
^{1}S	0	0	0	0	[Kr] 4d^{10}
^{3}D	6737	6131	5126	6564	[Kr] 4d^9 5s

Best agreement with experiment is obtained at the LDA level of theory. However, it is well know that LDA is unreliable for binding energies. Therefore, we have chosen the PBE functional for our further studies.

Our next study focuses on the particular numerical procedure for solving the Kohn-Sham equations. In deMon2k two different Kohn-Sham methods are implemented. In the first one the variational fitting of the Coulomb potential is used but the exchange-correlation matrix elements are calculated with the Kohn-Sham orbital density. This approach is sometimes named in the literature RI-DFT (Resolution-of-the-Identity Density Functional Theory). In the second method, that is computationally much more efficient, not only the Coulomb potential but also the exchange-correlation matrix elements are calculated with the auxiliary function density. This approach is named auxiliary density functional theory (ADFT) and permits the calculations of large systems and Born-Oppenheimer molecular dynamics simulation on the nanosecond time scale. Tables 2 and 3 compare the optimized bond lengths, vibrational frequencies, zero-point

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[a] Experimental data from C.E. Moore, Atomic Energy Levels, Vol. III, NSRDS-NBS35 Washington, D.C. 1971. The experimental ^{3}D energy refers to the ^{3}D$_3$ state.

energies, relative energies and binding energies per atom (ZPE and BSSE corrected) of the lowest lying triplet, singlet and quintet states of Pd_2 from RI-DFT and ADFT calculations employing the PBE functionals and the above described QECP18 and GEN-A2* auxiliary function set.

Table 2: RI-DFT/GEN-A2* optimized bond lengths, r_e, vibrational frequencies, ω_e, zero-point energies, ZPE, relative energies, ΔE, and binding energies per atom, BE, of the lowest lying triplet, singlet and quintet states of Pd_2.

Dimer	$r_e[Å]$	$\omega_e[cm^{-1}]$	Energies[meV]		
			ZPE	ΔE	BE
$^3Pd_2$	2.51	204	9	0	716
$^1Pd_2$	2.71	155	13	490	473
$^5Pd_2$	2.53	181	13	1982	-278

Table 3: ADFT/GEN-A2* optimized bond lengths, r_e, vibrational frequencies, ω_e, zero-point energies, ZPE, relative energies, ΔE, and binding energies per atom, BE, of the lowest lying triplet, singlet and quintet states of Pd_2.

Dimer	$r_e[Å]$	$\omega_e[cm^{-1}]$	Energies[meV]		
			ZPE	ΔE	BE
$^3Pd_2$	2.50	213	9	0.0	703
$^1Pd_2$	2.72	146	13	464	473
$^5Pd_2$	2.54	172	9	2016	-304

The comparison of Table 2 and Table 3 reveals that RI-DFT and ADFT optimized bond lengths of Pd_2 differ at most by 1 pm. The corresponding vibrational frequencies agree within 10 cm^{-1}. Relative energies and (corrected) binding energies per atom differ by no more than 30 meV. All these differences are far beyond the intrinsic accuracy of the used density functionals. Therefore, we have performed the Pd_{13} optimizations, frequency analyses and Born-Oppenheimer molecular dynamics simulations in the framework of the ADFT methodology.

Comparison of our ADFT Pd_2 results with experiment is rather satisfying. The estimated experimental bond length[7] of 2.47 Å is in good agreement with our optimized bond length of 2.50 Å. The agreement with the more accurate determined experimental vibrational frequency[8] of 210±10 cm^{-1} is excellent. This indicates that the ADFT structure and electronic state description is of good quality, comparable to CCSD(T) results[9]. However, the experimental binding energy estimate[10] of 366±130 meV is smaller than our calculated value. The observed overbinding is in the typical range for DFT transition metal calculations. Our previous studies of 3d transition metal dimers have shown that these errors can be mainly attributed to the atomic calculations[6] and, thus, do not jeopardize the accuracy of the molecular results.

2. Cluster Structures and Energies

Total energies [a.u.] and Cartesian coordinates [Å] of ADFT optimized Pd_{13} isomers. The (approximated) symmetry point group and molecular spin multiplicity are also given.

Energy: -1663.278095
Symmetry: C_s
Multiplicity: 1

Pd	1.011355	0.002926	1.025824
Pd	1.832291	0.002645	-1.819236
Pd	-0.238073	2.270997	1.560652
Pd	-1.616510	-0.003244	1.152215
Pd	-0.227833	-2.270741	1.562690
Pd	-2.471619	-2.258231	0.059322
Pd	1.952394	2.156449	-0.126805
Pd	-2.484017	2.249255	0.060063
Pd	-2.575955	-0.005765	-1.448242
Pd	1.957410	-2.150320	-0.127523
Pd	-0.342568	1.386240	-1.116803
Pd	-0.336122	-1.383023	-1.118374
Pd	3.539247	0.002813	0.336217

Energy: -1663.279198
Symmetry: C_s
Multiplicity: 3

Pd	1.022788	0.002862	1.050721
Pd	1.889379	0.004086	-1.807162
Pd	-0.266507	2.248613	1.532559
Pd	-1.652254	-0.015354	1.153729
Pd	-0.226775	-2.285300	1.527876
Pd	-2.461193	-2.267979	0.043731
Pd	1.978091	2.140804	-0.101848
Pd	-2.545231	2.218329	0.069121
Pd	-2.611775	-0.014016	-1.447808
Pd	1.966085	-2.106945	-0.125863
Pd	-0.344433	1.393801	-1.107324
Pd	-0.330837	-1.325054	-1.122482
Pd	3.582662	0.006154	0.334751

Energy: -1663.280080
Symmetry: C_s
Multiplicity: 5

Pd	1.044347	-0.002177	1.064987
Pd	1.920013	-0.001976	-1.738972
Pd	-0.273679	2.275386	1.433611
Pd	-1.682312	0.000607	1.163541
Pd	-0.277270	-2.278752	1.429803
Pd	-2.594903	-2.221326	0.046985
Pd	2.021373	2.167280	-0.089376
Pd	-2.591967	2.224518	0.046607
Pd	-2.570646	0.001273	-1.459328
Pd	2.020777	-2.166867	-0.089065
Pd	-0.314501	1.379960	-1.064113
Pd	-0.315781	-1.377865	-1.063990
Pd	3.614548	-0.000062	0.319311

Energy: -1663.283902
Symmetry: C_s
Multiplicity: 7 (**Global minimum**)

Pd	1.040108	-0.000463	1.059169
Pd	1.905564	-0.000448	-1.742663
Pd	-0.260675	2.328089	1.421585
Pd	-1.658238	0.000170	1.163567
Pd	-0.261442	-2.327813	1.421937
Pd	-2.588755	-2.230707	0.059758
Pd	2.018931	2.164124	-0.084403
Pd	-2.587634	2.231556	0.059554
Pd	-2.593709	0.000160	-1.437666
Pd	2.018796	-2.164258	-0.084846
Pd	-0.323630	1.371409	-1.072815
Pd	-0.324082	-1.371625	-1.072399
Pd	3.614769	-0.000193	0.309222

Energy: -1663.276074
Symmetry: C_s
Multiplicity: 9

Pd	1.051494	0.000087	1.080170
Pd	1.888637	0.003137	-1.765220
Pd	-0.269967	2.305379	1.478271
Pd	-1.641914	-0.001764	1.157350
Pd	-0.266708	-2.307922	1.477089
Pd	-2.577095	-2.198545	0.047271
Pd	1.999793	2.156416	-0.079412
Pd	-2.581808	2.194273	0.051981
Pd	-2.577545	-0.001320	-1.507417
Pd	2.004008	-2.155344	-0.079811
Pd	-0.325134	1.365359	-1.054900
Pd	-0.320985	-1.361852	-1.054015
Pd	3.617223	0.002096	0.248645

Energy: -1663.278279
Symmetry: C_{3v}
Multiplicity: 1

Pd	0.582713	1.519570	1.227204
Pd	2.974508	0.475662	1.166236
Pd	-1.897091	2.336911	1.168536
Pd	-0.000825	-0.001043	-1.047868
Pd	2.504099	-0.974213	-1.019293
Pd	-2.510313	0.947393	-1.026594
Pd	2.074594	1.698652	-1.029214
Pd	1.026208	-1.263393	1.228491
Pd	-1.075573	-2.809584	1.169038
Pd	-1.606125	-0.255143	1.227227
Pd	-2.096104	-1.683025	-1.019760
Pd	0.433673	-2.647339	-1.025442
Pd	-0.409766	2.655550	-1.018560

Energy: -1663.279087
Symmetry: C_{3v}
Multiplicity: 3

Pd	1.152260	1.041392	-1.284963
Pd	-0.665848	2.940921	-1.175347
Pd	2.861876	-0.958811	-1.168419
Pd	0.022720	0.013498	1.042310
Pd	-1.761649	1.996126	1.088415
Pd	1.807057	-1.958225	1.079973
Pd	0.865119	2.562904	0.959068
Pd	-1.570945	0.487214	-1.200631
Pd	-2.256520	-2.031798	-1.160332
Pd	0.320282	-1.597637	-1.222373
Pd	-0.801396	-2.545074	1.019428
Pd	-2.620753	-0.543122	1.043513
Pd	2.647798	0.592611	0.979359

Energy: -1663.279933
Symmetry: C_{3v}
Multiplicity: 5

Pd	1.230180	0.796241	-1.253961
Pd	-0.320339	2.943873	-1.255827
Pd	2.750617	-1.362104	-1.147284
Pd	0.030425	0.085519	1.038171
Pd	-1.538071	2.225581	0.987944
Pd	1.608470	-2.040136	1.143137
Pd	1.133837	2.487376	0.946777
Pd	-1.485224	0.565582	-1.254016
Pd	-2.489234	-1.860694	-1.079883
Pd	0.140608	-1.760821	-1.151478
Pd	-1.108806	-2.300565	1.166631
Pd	-2.742644	-0.159526	0.978245
Pd	2.790182	0.379674	0.881545

Energy: -1663.280263
Symmetry: C$_{3v}$
Multiplicity: 7 (local min. for C$_{3v}$)

Pd	-1.385310	0.693516	1.207951
Pd	-0.030251	2.988845	1.257820
Pd	-2.627909	-1.638916	1.105920
Pd	-0.001413	0.076649	-0.998429
Pd	1.310965	2.417306	-0.948659
Pd	-1.320552	-2.253928	-1.094640
Pd	-1.392478	2.381779	-0.928391
Pd	1.368107	0.724992	1.207945
Pd	2.666934	-1.575040	1.103850
Pd	0.021412	-1.719541	1.239483
Pd	1.384860	-2.211322	-1.103981
Pd	2.758058	0.098300	-1.018401
Pd	-2.752423	0.017362	-1.030468

Energy: -1663.273060
Symmetry: C$_{3v}$
Multiplicity: 9

Pd	-0.977717	1.338983	1.215880
Pd	1.316996	2.649683	1.209592
Pd	-3.221851	-0.049330	0.980455
Pd	0.174323	0.005853	-1.000332
Pd	2.449871	1.418095	-0.844307
Pd	-2.180056	-1.364154	-1.111330
Pd	0.085941	2.675134	-1.126516
Pd	1.462609	0.019182	1.346719
Pd	1.400958	-2.612394	1.206439
Pd	-0.935322	-1.373647	1.211754
Pd	0.157152	-2.668898	-1.123700
Pd	2.482855	-1.348763	-0.858042
Pd	-2.215759	1.310255	-1.106613

Energy: -1663.255457
Symmetry: ~I$_h$
Multiplicity: 1

Pd	0.006337	0.030757	-0.003447
Pd	2.108117	1.866547	0.006634
Pd	-1.219121	2.510101	-0.008039
Pd	0.335054	1.545347	-1.979875
Pd	-0.292678	-1.347710	-2.123756
Pd	-2.327248	0.396910	-1.337765
Pd	0.314877	1.543523	1.977292
Pd	2.302095	-0.488175	-1.321503
Pd	-2.315410	0.398203	1.350106
Pd	0.888302	-2.566865	-0.006390
Pd	-1.813951	-2.046304	-0.000672
Pd	2.298993	-0.487998	1.330549
Pd	-0.285365	-1.354336	2.116866

Energy: -1663.260749
Symmetry: ~I$_h$
Multiplicity: 3

Pd	-0.000039	0.010181	-0.001320
Pd	-1.751807	2.266964	-0.014103
Pd	1.769024	2.253963	0.014169
Pd	-0.010830	1.619123	1.906058
Pd	-0.024111	-1.408209	2.110881
Pd	2.322373	-0.059452	1.344996
Pd	0.023470	1.618923	-1.906124
Pd	-2.347970	-0.037682	1.317417
Pd	2.348233	-0.052693	-1.315606
Pd	-1.408407	-2.376114	-0.012255
Pd	1.390834	-2.386035	0.010805
Pd	-2.323820	-0.040154	-1.342960
Pd	0.013050	-1.408814	-2.111959

Energy: -1663.264681
Symmetry: ~I_h
Multiplicity: 5

Pd	-0.000893	0.033709	0.000482
Pd	-1.648712	2.179689	0.000153
Pd	1.544205	2.244555	0.003118
Pd	-0.037682	1.509883	2.099524
Pd	0.028194	-1.414184	2.150160
Pd	2.354151	0.025981	1.341153
Pd	-0.033400	1.509441	-2.099142
Pd	-2.357744	-0.078011	1.331852
Pd	2.358082	0.025071	-1.337070
Pd	-1.372042	-2.303948	-0.002091
Pd	1.477524	-2.243230	0.003651
Pd	-2.352090	-0.076950	-1.342722
Pd	0.040407	-1.412006	-2.149068

Energy: -1663.271370
Symmetry: ~I_h
Multiplicity: 7

Pd	-0.000465	-0.002192	-0.001038
Pd	0.041051	2.547629	0.611730
Pd	2.317922	1.308605	-0.532203
Pd	1.534194	0.709907	1.998400
Pd	0.091074	-1.673532	1.996294
Pd	2.352814	-1.328532	0.345850
Pd	-0.083130	1.680102	-1.985261
Pd	-1.349622	0.719823	2.112712
Pd	1.338176	-0.723130	-2.122165
Pd	-2.318451	-1.315870	0.532084
Pd	-0.048246	-2.546094	-0.602520
Pd	-2.347586	1.331132	-0.343510
Pd	-1.527732	-0.707847	-2.010373

Energy: -1663.278977
Symmetry: ~I_h
Multiplicity: 9 (local min. for ~I_h)

Pd	-0.000703	0.000019	-0.000003
Pd	2.352075	1.390076	-0.100241
Pd	2.341531	-1.404633	-0.107268
Pd	1.534926	-0.008287	2.145189
Pd	-1.323742	0.002557	2.262398
Pd	0.063988	-2.216488	1.366389
Pd	1.322781	-0.000922	-2.263263
Pd	0.074668	2.215156	1.368069
Pd	-0.080114	-2.215557	-1.367020
Pd	-2.340774	1.406828	0.109003
Pd	-2.350870	-1.393037	0.099443
Pd	-0.060387	2.216291	-1.367013
Pd	-1.533379	0.007997	-2.145684

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