Density-Functional and *Ab Initio* Computational Studies of Palladium Clusters

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Abstract

Nonlocal density-functional and correlated *ab initio* methods have been used to compute singlet–triplet separations for the Pd atom and Pd_2, as well as the dissociation energies of the latter in its ground and first excited states. The results are in good agreement with the available experimental data and with other high-level calculations. Single-point local density-functional computations were carried out for Pd clusters up to Pd_{22} (1012 electrons). The interaction energy per Pd — Pd bond appears to be approaching a limiting value for Pd_{22}. © 1993 John Wiley & Sons, Inc.

Introduction

We are interested in applying density-functional theory (DFT) to small clusters of transition metal atoms. One of our objectives is to determine how large a cluster is needed to realistically simulate a metal surface, in order to permit the investigation of chemisorption and catalytic processes; and to determine the ground state atomic and electronic structure of small transition metal clusters.

In the present work, we have focused specifically upon palladium, and have proceeded on two levels: (a) We have compared sophisticated nonlocal DFT and *ab initio* methods in computing the singlet–triplet separations for the palladium atom and the Pd_2 molecule, as well as the bond length and dissociation energy of the latter in each state; and (b) we have used a local DFT approach to carry out single-point runs on clusters as large as Pd_{22} (1012 electrons).

Methods

Density-functional theory [1–4], as it has been applied in this investigation, is based on the Hohenberg–Kohn theorem [5] and the Kohn–Sham procedure [6]. In the latter, the total energy of an N-electron system (as would be obtained by solving the Schrödinger equation exactly) is found by minimizing, with respect to the electronic density $\rho(\mathbf{r})$, the total energy functional $E[\rho]$,

$$E[\rho] = \int v_{\text{ext}}(r)\rho(r)\, dr + T_s[\rho] + V_{\text{class}}[\rho] + E_{xc}[\rho] . \qquad (1)$$

$V_{\text{ext}}(\mathbf{r})$ is the external potential due to the nuclei, $T_s[\rho]$ is the kinetic energy of a hypothetical set of non-interacting electrons having the same density $\rho(\mathbf{r})$ as the

system under consideration, and $V_{class}[\rho]$ is the classical energy calculated using the density $\rho(\mathbf{r})$.

$$V_{class}[\rho] = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \tag{2}$$

The exchange–correlation functional, $E_{xc}[\rho]$, is expressed exactly in terms of the adiabatic connection variable λ by Eq. (3):

$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle \, d\lambda - V_{class}[\rho]. \tag{3}$$

The functions Ψ_λ are the solutions of,

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda \tag{4}$$

where,

$$\hat{H}_\lambda = \hat{T} + \hat{v}_\lambda + \lambda \hat{V}_{ee}. \tag{5}$$

In Eq. (5), the electron–electron interaction operator, $\hat{V}_{ee}$, is linearly scaled from zero to one by the variable λ in a manner such that v_λ yields the same $\rho(\mathbf{r})$ for any λ in the interval [0,1]. (According to the Hohenberg–Kohn theorem, the potential determines the density [5].)

The energy quantity E_{xc} as given by Eq. (3) is clearly not equivalent to the sum of the exchange and correlation energies as defined in *ab initio* formalism. Unfortunately, the expression for $E_{xc}[\rho]$ in Eq. (3) can only be evaluated in special cases. One of these is an uniform electron gas (jellium), for which exact ground-state solutions have been obtained by stochastic simulations [7], from which functionals have been constructed, primarily by fitting procedures [8]. These functionals correspond to the local density approximation. First-order corrections can be made using gradients of the density, resulting in so-called nonlocal approximations [1,2].

For the Pd atom and for Pd_2, we have used the sophisticated nonlocal exchange-correlation functional of Perdew and Wang, the generalized-gradient approximation (GGA) [11,12]. This was developed entirely from first principles, and has no fitted parameters. We have recently coded this functional into the DFT program deMon [13,14]. The single-point runs on Pd clusters were carried out with the DFT program DMol [15], which uses a local-density approximation [16]. We have used the standard double numerical (DN) basis set. The *ab initio* results that we report were obtained with Gaussian 92 [17].

Results

Pd Atom

The standard deMon Gaussian DZVPP basis set for Pd, (18s, 12p, 9d) contracted to (6s, 5p, 3d), yields a singlet–triplet separation of 33.5 kcal/mol, which differs considerably from the experimental 18.8 kcal/mol [18]. Accordingly we used Huzinaga's (17s, 11p, 8d) basis set [19], uncontracted, to compute the singlet–triplet

separation by both *ab initio* and DFT procedures. The two DFT calculations were carried out with the Perdew–Wang $E_{xc}[\rho]$ functionals GGA–PW86 [9,10] and GGA–PW91 [11,12]. The results are in Table I.

Most of the *ab initio* correlated results and both of the DFT are within 3 kcal/mol of the experimental value. It is seen that the effect of including the core electrons can be quite significant, as much as 5.3 kcal/mol. It is relevant to mention that a QCI (full core) calculation was terminated after having used more than one hour of CPU time on a CRAY C-90 for only two iterations (out of possibly 15) of the triple substitutions; in contrast, the DFT calculations despite slow convergence (more than 1500 iterations for the triplet) required only about 10 min.

Pd_2

Initial results obtained with the DZVPP basis set were qualitatively incorrect, so we have continued with the Huzinaga [19]. Our computed bond lengths, total energies and dissociation energies for the triplet ground state and the first singlet excited state of Pd_2 are given in Table II, as are the singlet–triplet separations, T_e. Experimental and other calculated data are also included. Our DFT–GGA–PW86 ground state dissociation energy and triplet–singlet separation are in good agreement with the MCSCF(CASSCF)MRSDCI results and with one of the experimental values for D_e.

Pd Clusters

The Pd clusters that were investigated are shown in Figure 1. They were given geometries corresponding to the [111] surface of the metal, with the closest inter-

TABLE I. Calculated energies of the singlet ground state and first excited triplet state of the palladium atom, using the Huzinaga (17s, 11p, 8d) basis set.

Method	Singlet (hartrees)	Triplet (hartrees)	Separation (kcal/mol)
Hartree–Fock	−4937.79120	−4937.78582	3.4
MP2 (frozen core)	−4937.91174	−4937.87904	20.5
MP2 (full core)	−4938.75759	−4938.71649	25.8
MP3 (frozen core)	−4937.90090	−4937.87540	16.0
MP3 (full core)	−4938.68426	−4938.66039	15.0
MP4SDQ (frozen core)	−4937.90689	−4937.87748	18.5
MP4SDQ (full core)	−4938.71916	−4938.68446	21.7
QCISDt (frozen core)	−4937.90824	−4937.87999	17.7
DFT–GGA–PW86	−4940.67375	−4940.64130	20.4
DFT–GGA–PW91	−4940.66042	−4940.62611	21.5
Experimental[a]			18.8
MCSCF(CASSCF)/FOCI + RCI[b]			13.8

[a] Reference [18].
[b] Reference [20].

TABLE II.   Results for the palladium dimer ground state triplet and first excited state singlet using the (17s, 11p, 8d) basis set.

| Method	Triplet			Singlet			Separation T_e (kcal/mol)
	Energy (hartrees)	R_e (Å)	D_e (kcal/mol)	Energy (hartrees)	R_e (Å)	D_e (kcal/mol)	
Hartree–Fock	−9875.57302	2.78	5.9				
MP2 (frozen core)	−9875.81501	2.46	−5.3	−9875.82866	2.9	3.3	−8.6
DFT–GGA–PW86	−9881.37740	2.62	18.8	−9881.36716	2.7, −2.8[d]	12.3	6.4
Experimental[a]			16.9, 26.0				
MCSCF(CASSCF)MRSDCI[b]		2.48	19.6		2.87		3.6
DFT (model core potential)[c]		2.46	31.3		2.64	21.9	9.5

[a] Reference [21].
[b] Reference [22].
[c] Reference [23].
[d] A very shallow minimum was obtained.
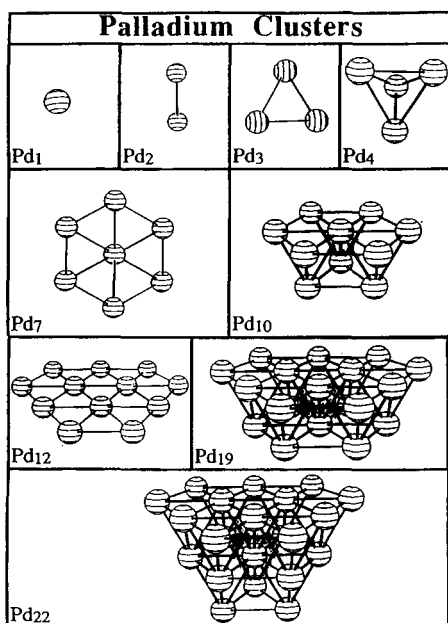
Figure 1.   Palladium clusters that were studied using a local density-functional theory approach.

TABLE III. Local density-functional theory results for palladium clusters.

| Cluster | Number of Pd — Pd bonds | Energy (hartrees) | $\Delta E = E(Pd_n) - nE(Pd)$ | | ΔE per Pd — Pd bond (kcal/mol) |
			(hartrees)	(kcal/mol)	
Pd_1	0	−4935.1926	−0.0	0.0	—
Pd_2	1	−9870.4412	−0.056	−35.1	−35.1
Pd_3	3	−14805.7079	−0.130	−81.6	−27.2
Pd_4	6	−19741.0160	−0.2456	−154.1	−25.7
Pd_7	12	−34546.8208	−0.4724	−296.5	−24.7
Pd_{10}	24	−49352.7822	−0.8561	−537.2	−22.4
Pd_{12}	24	−59223.2213	−0.9099	−571.0	−23.8
Pd_{19}	57	−93770.5585	−1.8988	−1191.5	−20.9
Pd_{22}	69	−108576.53	−2.29	−1438.5	−20.8

atomic distance in each case being set equal to the experimentally determined 2.75 Å [24]. The calculated total and interaction energies are given in Table III.

The dissociation energy of Pd_2 is predicted from Table III to be 35.1 kcal/mol, which is considerably greater than our DFT–GGA–PW 86 value in Table II, 12.3 kcal/mol. This could reflect both the difference in bond length and also the well-known tendency of local-density approximations to overestimate dissociation energies [25–27]. However a key point that emerges from Table III is that the interaction energy per bond appears to be nearing a limiting value for Pd_{22}. This suggests that clusters of this size may be reasonable models for a metal surface (including the underlying atoms).

Discussion

We have demonstrated the feasibility of local density-functional calculations on systems having as many as 1012 electrons (Pd_{22}). At the local/DN level, 660 basis functions are required for the latter computation. The total energy is in the neighborhood of −108576 hartrees. At this order of magnitude, the error in the energy due to the use of REAL*8 precision is about 6 kcal/mol. The use of REAL*16, which would solve the problem due to truncation in the floating point operations, is not practical because there are not commercial floating point processors of 128 bytes; accordingly the REAL*16 arithmetic must be software-implemented. Machines like the CRAY YMP then require about 10 times more CPU time to process REAL*16 operations. This is in addition to the inherent problem, in these Pd clusters, of a large number of low-lying states near the ground state, which makes the SCF convergence very slow and tedious. The convergence problem is independent of the program. On the CRAY YMP8-864, each SCF cycle required 764 seconds of CPU time; the number of cycles needed for a respectable energy was about 20, and much more for a good density. About 500 Mbytes of scratch disk space were required, which is not excessive in view of the size of the system.

Despite these figures, there is reason for optimism. With massively parallel computers, turn-around times are reduced by at least one order of magnitude. DFT

codes are more vectorizable than are *ab initio,* and run more efficiently by a factor of 3 to 5. This efficiency can be made much higher in massively parallel computers. DFT codes are still in development, and improvements can be anticipated.

Acknowledgment

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