Self-Consistent-Field Potential-Energy Surfaces for Hydrogen Atom Pairs within Small Palladium Clusters

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Abstract

An ab initio electronic structure study is presented of hydrogen-hydrogen interactions in an electronic environment perturbed by the presence of palladium atom clusters. In particular, we investigated changes in the interatomic potential when the atomic centers are trapped inside an *fcc* palladium octahedral hole and when they are separated from each other by a (111) plane of palladium atoms. The (111) plane was modeled with a cluster of three palladium atoms. Self-consistent field (scF) level calculations were performed, and palladium atom pseudopotentials were employed to make the systems studied computationally tractable. For pairs of atoms placed within the octahedral hole, various lines of approach were considered [along the (100), (110), and (111) directions]. Lattice deformations and electronic excitations were examined for their effect on the interatomic potential.

I. Introduction

Although the controversial claims of cold fusion by Fleishman et al. [1] and Jones et al. [2] sparked our initial interest in electronic screening within Pd lattices, the research presented here is of broad and fundamental importance, because of the catalytic, superconducting, and absorptive properties of Pd(s) [3–5]. We view the present work as a contribution to the electronic structure of palladium-hydrogen systems (for an overview of prefusion studies carried out on palladium-hydrogen systems, see [6]). In it, we have investigated the ground electronic states of PdH and Pd_2H_2 , singlet and triplet states of Pd_6H_2 and Pd_3H_2 , and electronic states resulting from various deformations of the Pd_6 octahedral hole containing a H_2 molecule.

Mintmire et al. [7] carried out local-density functional theory calculations on a system of 108 palladium atoms in an *fcc* structure with a single hydrogen atom located in each octahedral hole. They seeded this structure with first one and then two *additional* hydrogen atoms and found that the relaxed structure was such that the hydrogens repelled each other with no potential energy minimum

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found. Mintmire et al. also performed $X\alpha$ calculations with the hydrogens constrained to approach each other along the (111) direction.[†] Again, only repulsive H₂ interactions were discovered.

Sun and Tománek [8] and Wang et al. [9] employed density functional calculations to show that a minimum exists in the D_2 curve at 1.76 au provided that the deuterium molecule was aligned in the (100) direction. This distance is even greater than the bond length of gaseous D_2 , which is approximately 1.4 au (1 au ≈ 0.529 Å).

Further density functional calculations were carried out by Dunlap et al. [10] on Pd_6H_2 and Pd_4H_2 . Although they employed two separate energy functionals and allowed for expansion of the Pd lattice, they found no evidence for an increased HH binding energy over free H_2 . The claim that the binding energy of HH is weakened with a palladium lattice was again supported by Christensen et al. [11], who carried out calculations within the local-density approximation for H_2 in a homogeneous electron gas. Halley and Vallés [12] carried out molecular dynamics simulations on PdD_n with n = 1, 3, 4, and 5 in a static *fcc* lattice of 108 Pd atoms with periodic boundary conditions.

In Section II, we use ab initio methods to look for states of H_2 trapped within a palladium octahedral hole that might give rise to a less repulsive interatomic potential. In Section III, a summary and discussion are presented.

II. Electronic Structure Calculations

In the following sections, we consider the ab initio evaluation of the interaction potential for HH within a palladium octahedral hole and with Pd_3 .

A. Method and Systems Studied

Choice of Basis Sets: All the calculations presented are of the ab initio scF level. For most of the systems studied, the choice of basis sets was as follows: for palladium, the (1s, 1p, 1d) Hay and Wadt 10-electron pseudopotential basis with relativistic corrections [13]; and for hydrogen, the $(6-311G^{**})$ Pople basis [14]. For our study of Pd₃H₂, we chose to use the (2s, 2p, 2d) double-zeta Hay and Wadt 10-electron pseudopotential basis with relativistic corrections [13]. These calculations were performed using the MESS Kit (Molecular Electronic Structure Kit) software modules.[‡]

[†]The (111) directions may be visualized as follows: The octahedral Pd hole is created by six Pd atoms, each of which lies at the center of the face of a cube. The (111) direction pass is defined by a ray that passes through the center and a corner of the cube.

⁴The Utah MESS Kit software was written during 1986–1990 primarily by R. A. Kendall, E. Earl, R. Hernandez, H. L. Taylor, D. O'Neal, J. Nichols, M. Hoffmann, M. Gutowski, K. Bak, J. Boatz, M.W. Feyereisen, W. Xiao, and J. L. Anchell. The code was written in a highly modular format, so that improvements in any module or additions of new modules that provide added functionality are facilitated. VAX VMS, Cray CTSS, SUN, Multiflow, RS6000, and FPS versions are available.

Systems Studied: The molecular systems studied in this work are PdH, Pd_2H_2 , Pd_3H_2 , and Pd_6H_2 . PdH was chosen for study to assess the quality of our basis set. Pd_2H_2 provided insight into the elementary interactions between palladium and the H_2 molecule. Pd_6H_2 was studied to model the nearest-neighbor interactions between the nuclei of two hydrogens found within an octahedral hole of solid palladium. The system Pd_3H_2 was chosen to model the interaction of two hydrogens approaching each other from opposite sides of the (111) surface of the palladium lattice.

HH Cohesion Energy: We define the HH interatomic potential, V'(R) by

$$V'(R) = E(Pd_m H_n) - E(Pd_m) - nE(H),$$
 (1)

where $E(Pd_mH_n)$ is the total energy of the palladium lattice plus hydrogen atoms, $E(Pd_m)$ is the energy of the palladium lattice, and E(H) is the energy of one hydrogen atom. V'(R) is also known as the negative of the cohesion energy [8]. In this work, m = 1, 2, 3, 6 and n = 1, 2. The cohesion energy may be thought of as the free, or gas phase, H_2 interaction energy plus the perturbation to this interaction energy brought about by the presence of palladium atoms.

Counterpoise [15] corrections were included for the PdH and Pd_2H_2 calculations and for the lowest singlet states of the Pd_6H_2 systems. Counterpoise corrections were *not* included for the Pd_6H_2 electronic excited states, because, in lieu of carrying out intractable multiconfiguration calculations on the systems studied, it is not obvious what the dissociation products of the Pd_6H_2 electronic excited states are. On the other hand, we have assumed that as the HH internuclear distance, R, goes to infinity that the lowest singlet state of the Pd_6H_2 system dissociates to the closed-shell ground electronic state of Pd_6 and the ground state of two hydrogen atoms. This assumption enabled us to carry out counterpoise corrections for our lowest singlet-state calculations. For Pd_3H_2 , we used a double-zeta basis set, which reduced the error from basis-set superposition to a relatively small value of a few hundredths of an electronvolt. Consequently, no counterpoise correction was applied to this system.

B. Results

1. PdH: To assess the quality of our basis and the level of calculation, we compare our calculation of the ground ${}^{2}\Sigma^{+}$ state of PdH to the all-electron twoconfiguration MCSCF nonrelativistic calculations of Bagus and Björkman of the same state [16], to the complete active space/first-order configuration interaction followed by relativistic configuration interaction calculations (RCI) on the ${}^{2}\Sigma^{+}_{1/2}$ state carried out by Balasubramanian et al. [17], and to spectroscopic experimental results [18]. To be consistent with the above sources, we enforce the dissociated state of palladium to be of ${}^{1}\Sigma(d^{10})$ symmetry. In Table I, our results and those cited above for the equilibrium bond distance, R_{e} , and the dissociation energy, D_{e} , of PdH are listed. The tabulated values of R_{e} and D_{e} indicate that the present method that employs pseudopotentials has closer agreement with relativistic calculations and experimental results than does the all-electron two-

	Present work	TCMCSCF [16]	rci [17]	Exp. [18]
Ground state	² Σ +	² Σ ⁺	${}^{2}\Sigma_{1/2}^{+}$	² Σ ⁺
R_{ϵ} (au)	3.0	3.11	2.89	2.90
D_e (eV)	2.29	1.39	2.21	3.3

TABLE I. Equilibrium bond lengths and dissociation energies obtained for PdH.

configuration MCSCF. This somewhat fortuitous result indicates that the present calculations should be judged acceptable.

2. Pd_2H_2 : The primary aim of our investigation is to search for an arrangement of palladium atoms that might increase the cohesion energy between the hydrogen atoms at short HH distances. Such an arrangement would decrease the classical turning point, R^* , and thus allow for greater tunneling than in free hydrogen.

To simplify the problem, we start with an HH pair with a bond length fixed at R = 0.6 au. For free H₂, the Born-Oppenheimer potential at this distance is repulsive. We next consider two geometries with the palladium atoms equidistant from the center of the H-H bond. In the collinear arrangement, the Pd atoms lie along the H-H bond axis, $(D_{\infty h}$ symmetry). In the transverse configuration, the palladiums are at right angles to the H-H bond $(D_{2h}$ symmetry). We then calculated the HH interatomic potential as a function of the distance R_{PdH} between the hydrogen and the nearest-neighbor palladium.

For the collinear geometry, the electronic state of Pd_2H_2 and the reference lattice, Pd_2 , which include hydrogen atoms ghost functions, was of ${}^{1}\Sigma_{g}^{+}$ symmetry. For the transverse geometry, the electronic states of both Pd_2H_2 and the reference lattice were of ${}^{1}A_{g}$ symmetry.

The results, which are plotted in Figure 1, show clearly that at no distance do the two palladiums lower the cohesive energy relative to the cohesive energy of free H_2 . The effect of the palladiums only serves to create a greater repulsion between the hydrogen atoms.

3. Pd₆H₂: Ground Singlet States of Pd_6H_2 . We chose three different geometries to study the ground electronic state of an HH pair trapped within an octahedral hole. The lattice constant of the *fcc* structure was taken to be 7.35 au to match the experimentally determined value [19]. The hydrogens were allowed to approach each other along the (100), (110), or (111) directions. For the (100), (110), and (111) HH pair orientations, we studied the closed-shell ${}^{1}A_{1g}$, ${}^{1}A_{g}$, and ${}^{1}A_{1g}$ electronic states, respectively.

We calculated the reference lattice energy, $E(Pd_6)$, appearing in Eq. (1) in the closed-shell ¹A state.[§] For bulk palladium, energy-band calculations give valence

⁶Our scF level calculations revealed that some triplet states of the Pd₆ cluster are slightly lower in energy than the lowest-energy closed-shell state. However, the Pd₆ energy was only needed to define the zero reference for the cohesion energy as shown in Eq. (1). For consistency, we have used the closed-shell Pd₆ energy as the reference energy for all systems involving six palladium atoms throughout the paper.



Figure 1. H_2 interatomic potential for both the collinear and transverse geometries of Pd_2H_2 as a function of Pd-H distance.

d populations of 9.63 [20]. To approximate this large population, we chose the symmetry of the molecular orbitals composing the single Slater determinant, so as to correspond to the 30 symmetry-adapted basis functions arising from linear combinations of the five d functions centered on each Pd atom in the lattice.

We tested this assignment of the orbital symmetries for the lowest-energy singlet configuration by calculating the sCF energy and wave function without explicit use of symmetry (i.e., the sCF algorithm assumed C_1 symmetry for the cluster).

For the Pd_6H_2 we used the molecular orbital symmetry assignments for the lattice, which was described in the preceding paragraphs, and also included one extra doubly occupied orbital that transforms according to the completely symmetric representation. Correctness of the resulting electronic configuration was again tested via a parallel C_1 calculation.

The intermolecular potentials of the Pd_6H_2 clusters in their lowest singlet states as a function of HH internuclear distance are shown in Figure 2. This fig-



Figure 2. Lowest singlet-state intermolecular potentials in Pd₆H₂ as a function of internuclear distance for H₂ oriented in the (100), (110), and (111) directions.

ure is essentially the same as the Figure 1 that appears in the work by Dunlap et al. [10], in which local density functional theory was used to study the same system. At large HH internuclear separation, the cohesion energies in all three orientations is greater than the cohesion energy of free H₂. This is consistent with our knowledge that palladium metal is able to absorb large amounts of hydrogen and that saturated palladium has less than one (approximately 0.6) hydrogen atom per octahedral hole; that is, as long as the hydrogens are far enough apart, they are energetically more stable within the lattice than free and bound to each other. In the (100) direction, the interatomic potential reveals a minimum at 1.7 ± 0.1 au. This is in agreement with Sun and Tománek's [8] result in which they obtained a minimum at 1.76 au.

Although it is dissociative, the path of least resistance at long distances $(R \approx 2.9 \text{ au})$ is along the (111) direction. This result is in accord with molecular dynamics simulations [21, 22] that show that the favored path for diffusion of hydrogen in palladium is from octahedral to tetrahedral to octahedral site. [The octahedral-to-tetrahedral path is in the (111) direction.] However, we observe that the value of R^* for free H₂ is less than the value of R^* for all three of the systems studied that include palladium atoms.

Intermediate calculations showed that if the counterpoise corrections were not included one would have quite contrary results; that is, one would observe that the lattice-hydrogen system was conducive to allowing hydrogens to approach closer together that in the free H_2 case. However, the BSSE is quite large—on the order of 2 eV.^I

In Figures 3-5, we have plotted orbital energies as a function of HH internuclear distance, R, of the (100), (110), and (111) lines of the HH approach. There are several salient features common to each of these figures. First, the lowestlying molecular orbital has dominant atomic orbital (AO) contributions from the $1s_{H} + 1s_{H}$ orbitals centered on the hydrogens. This is like the bonding σ molecular orbital in free H₂. The orbital of next lowest energy is dominated by the linear combination $1s_H - 1s_H$. This is like the antibonding σ^* LUMO in free H₂. However, in this case, the orbital is doubly occupied, and so in a local picture of the H₂ molecule inside of the Pd₆ lattice, one could say that the H₂ has a bond order of zero. As the HH bond length is decreased, the energies of the " σ " and " σ^* " orbitals diverge rapidly and the " σ " orbital drops at a precipitous rate. At very short distances (e.g., $R \approx 0.6$ au), the " σ^* " orbital begins to cross into the Pd lattice band.[#] Interestingly, the LUMO in all cases shown is of the same symmetry as the " $\sigma^{*"}$ molecular orbital. Above the LUMO in energy lies an orbital whose dominant AO contribution is from $2s_H + 2s_H$. Although the other virtual orbitals are increasing in energy as R decreases, the energy of this particular vir-

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The basis-set superposition error could have been minimized by employing a larger basis set, such as the Hay and Wadt double-zeta pseudopotential basis. However, the size of the systems studied limited the number of basis functions employable.

[&]quot;By "palladium lattice band," we mean a manifold of orbital energies that are closely spaced and whose dominant AO contributions are from atomic orbitals centered on the palladium lattice atoms.

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R (a.u.)

Figure 3. Lowest singlet-state molecular orbital energies of the Pd_6H_2 cluster for the (100) orientation of H_2 . The symmetry of the cluster is isomorphic to the point group D_{4h} .

tual orbital decreases monotonically. At very short distances, ($R \approx 0.2$ au), this orbital's energy decreases so much that it eventually becomes the LUMO.

Triplet Electronic States of Pd_6H_2 . It is possible that there exists excited states that will allow the HH pair in the octahedral hole to approach closer together than in free H_2 . For this investigation, we chose to limit our study to the (100) and (111) orientations of the HH pair. We will consider two classes of triplet states. The first arises from excitations of a single electron from the HOMO to the LUMO. For the (100) and (111) orientation, these are states of ${}^{3}A_{1u}$ and ${}^{3}B_{1g}$ symmetry, respectively. These states were chosen simply because they are energetically easily accessible.

A second class of triplet states involves excitation from the HOMO to the virtual orbital dominated by the $2s_H + 2s_H$ combination of AOS. For the (100) and (111) orientation, these are states of ${}^{3}B_{1g}$ and ${}^{3}A_{2g}$ symmetry, respectively. For both of these states, the electron is excited to an orbital possessing a_{1g} symmetry. These states are attractive to our investigation for two reasons: First, at short HH dis-



Figure 4. Lowest singlet-state molecular orbital energies of the Pd_6H_2 cluster for the (110) orientation of H_2 . The symmetry of the cluster is isomorphic to the point group D_{2h} .

tances, the virtual a_{1g} orbitals in question become the LUMOS, so that for small R it should be least energetically expensive to excite electrons to these states. Second, investigation of the shape of these molecular orbitals suggests that they have qualities conducive to screening of the H⁺ H⁺ interaction. Figure 6 is a cartoon that describes the orientation of the hybridized orbitals for these two a_{1g} orbitals in question. In both cases, one sees that there is a buildup of the electronic density between the two hydrogens plus a node in the density between the palladium lattice and the hydrogens. The increased density between the hydrogen nuclei should provide shielding to the H⁺ H⁺ Coulombic interaction. By exciting an electron to the bonding a_{1g} orbital, we improve the HH "bond order" from zero to one-half.

The interatomic potentials as a function of R for the above-mentioned excited states are shown in Figure 7. For the (100) orientation of the HH pair, much of what we expected can be observed in these figures. At large values of R, the excited state that arises from excitation to the a_{2u} LUMO has a greater HH cohesion

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Figure 5. Lowest singlet-state molecular orbital energies of the Pd_6H_2 cluster for the (111) orientation of H_2 . The symmetry of the cluster is isomorphic to the point group D_{3d} .

energy than those excited states resulting from a promotion of an electron to the bonding a_{1g} virtual orbital. As R decreases, this discrepancy in energy is reduced—this is expected as we have seen that the a_{1g} orbital energy declines as the HH distance is shortened. This trend continues until at very short distances (not shown in the figure due to limitations on the scale and the resolving power of the graph) the interatomic potential of the ${}^{3}B_{1g}$ state becomes lower in energy than the ${}^{3}B_{2u}$ state. For the (111) orientation of the HH pair, the cohesion energy of the "bonding" ${}^{3}A_{2g}$ state is, surprisingly, everywhere greater than the ${}^{3}A_{1u}$ state.

For the (111) orientation of the HH pair, no minima are observed for either triplet state. No minimum was observed for the (111) orientation of the HH pair in the ground singlet state either. For the ${}^{3}B_{2u}$ state of the cluster with the HH pair oriented in the (100) direction, a minimum appears at 1.7 au, which is the same internuclear distance as obtained for the singlet state. The ${}^{3}B_{1g}$ state shows a minimum at 1.5 au. This bond-length shortening relative to the singlet state



Figure 6. (a) Virtual a_{1g} orbital for the Pd₆H₂ cluster with H₂ oriented in the (100) direction; (b) virtual a_{1g} orbital for the Pd₆H₂ cluster with H₂ oriented in the (111) direction.

may be a result of the screening of the nuclei from the electron in the a_{1g} orbital discussed above.

Even though in the (100) case we were able to screen the nuclei, so as to reduce the HH bond length, the total energy of the excited state is significantly higher. Therefore, at a given energy for the colliding hydrogens, the classical turning point for the excited states maintains the hydrogens further apart than the classical turning point of the ground state.

4. Pd₆ Lattice Distortions: In the following two sections we consider states of the Pd_6H_2 system in which the palladium lattice has been distorted: Of course,

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Figure 7. Triplet states intermolecular potentials as a function of internuclear distance for the hydrogen molecule oriented in the (100), (111), and (110) directions.

lattice distortions should be kept within reasonable thermodynamic accessibility. From Figure 4 in a paper on molecular dynamics simulations of hydrogen in palladium by Gillan, we estimate that the root mean square displacement of the palladium lattice is approximately 0.2 au [22]. Lattice displacements of Pd much greater than 0.2 au are presented mainly for theoretical curiosity. Also, since pseudopotentials have been employed in these calculations, the distortions must be such that the outer electron density on one atom does not penetrate too deeply into the core of a neighboring palladium atom. We tested the pseudopotential for Pd₂ and found that the electronic energy was well behaved when the palladium-to-palladium distance was greater than 2 au. We also tested the basis for PdH and found that the basis worked well when the palladium-to-hydrogen distance was greater than 1.5 au. None of the systems presented below had geometries that transgressed these boundaries.

Static Lattice Distortion. We have investigated normal-mode displacements of the lattice palladiums. In particular, we have studied the breathing mode of the lattice (a mode in which each of the palladiums is displaced equally toward the center of the octahedral hole) and the asymmetric stretching mode (a mode in which four palladiums contained in a plane are moved toward the center of the octahedral hole, and the remaining two palladiums atoms are displaced an equal distance away from the center of the octahedral hole, and vice versa). The (100) and (111) orientations of the HH pair were considered in both singlet and triplet electronic states. These distortions are held fixed in time as the hydrogen atoms approach each other, so we refer to it as a "static lattice distortion."

For brevity, we present only three representative results. In Figure 8 are shown the singlet-state interatomic potentials for the HH pair in the (111) orientation in which each of the palladium atoms has undergone a breathing mode displacement of 0.2, 0.4, or 0.8 au. One should notice that the cohesion energy is everywhere negative; that is, the palladium lattice with hydrogen atoms in-

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Figure 8. Lowest singlet-state interatomic potential of H_2 oriented in the (111) direction in which the lattice has undergone breathing mode distortions of 0.2, 0.4, and 0.8 au.

finitely far away is more stable than any possible arrangement of HH within the lattice. This result held for all the lattice distortions investigated. This does not mean, however, that such a geometrical arrangement is impossible. In fact, the existence of a minimum at about 1.2 au in all three cases indicates that if the HH pair is found in such a state then there is a sizable activation barrier to freeing the hydrogens from within the octahedral hole. It has already been shown that if the hydrogens are far enough apart in the undistorted octahedral hole that containment is energetically stable. So, by a quick rearrangement of the surface, e.g., dendrite formation as suggested by Bockris et al. [23], the hydrogens might be found kinetically trapped within just such a distorted octahedral hole, regardless of thermodynamic instability.

In agreement with the local density calculations of Wang et al. [9], these calculations suggest that significant bonding may be occurring between the hydrogens and their nearest-neighbor palladium atoms. From the point of view of a single hydrogen atom in the Pd_6H_2 molecule, bonding may occur with the neighboring hydrogen or with palladiums atoms in the lattice. The bond strength of PdH is not negligible compared to that of H_2 . Our scF study gave a dissociation energy of 2.9 eV for PdH, which is comparable to the H_2 dissociation energy of 4.75 eV.

One can make an educated guess as to what the equilibrium geometry of bound states of the Pd_6H_2 cluster should be with respect to the position of the hydrogens. Based on the two-body interaction energies of HH and PdH, one would predict the geometrical minimum should be one such that the distance from hydrogen to its nearest-neighbor palladium, R_{PdH} , is as close as possible to the equilibrium bond length of PdH, and the HH separation, R, is close to the equilibrium bond length of free H₂.

For the lattice deformations of 0.2 and 0.4 au, the equilibrium value of the hydrogen-to-nearest-neighbor palladium distance, R_{PdH} , is 2.8 and 3.0 au, respectively. These values are comparable to the equilibrium bond length of 3.0 au recorded earlier for PdH. By comparison, R_{PdH} for the 0.8 au breathing mode distortion is geometrically restricted to be less than 2.85 au—this distance

being possible only when both hydrogens are situated exactly at the center of the octahedral hole. Instead, for the 0.8 au distortion, the need to keep the hydrogens far enough apart to avoid strong nuclear repulsion of the hydrogens forced $R_{\rm PdH} = 2.5$ au—an energetically less favorable position with respect to the three nearest-neighbor palladium to hydrogen two-body interactions. These observations explain why the cohesion energy found for the 0.8 au distortion is so much weaker than for the 0.2 or 0.4 au breathing-mode distortions.

Dynamic Lattice Distortion. In the previous section, we saw that the HH pair appeared to be most stable in the octahedral hole when R_{PdH} had values near 3.0 au, the equilibrium bond length obtained for PdH. Additionally, in our study of the Pd₆H₂ ground state with the HH pair oriented in the (100) direction, we discovered a minimum in the HH interatomic potential at R = 2.8 au. This corresponds to a value of R_{PdH} equal to 2.8 au. Also, for the corresponding ${}^{3}B_{1g}$ excited-state calculation, the hydrogen-to-nearest-neighbor-palladium distance was discovered to be 2.9 au.

These observations motivated the next series of calculations in which we moved the hydrogen atoms closer together and at the same time distorted the lattice so as to maintain the "optimal" value of R_{PdH} . The interaction we wanted to model resembled that of a nut and nutcracker—the HH pair being the nut and the moving palladium lattice resembling the nutcracker. Since the lattice distorts in time as the hydrogen atoms approach each other, we refer to this as a "dynamic lattice distortion."

In practice, we moved the two palladiums that lie on the (100) line toward the center of the octahedron while moving two hydrogens in concert along this same line. For the triplet state, we maintained the hydrogen-to-moving-palladium distance fixed at 2.9 au, and for the singlet state, this distance was held fixed at 2.8 au. These distances were chosen so as to coincide with the equilibrium R_{PdH} values obtained for the triplet and singlet Pd₆H₂ calculations discussed above. The cohesion energy was determined by calculating the lattice energy at each new geometry as the HH pair were brought together.

The results of these calculations are shown in Figure 9. At any given energy, the classical turning points are such as to maintain the hydrogens further apart than they would be able to approach in free H_2 . A weak attractive minimum is seen at a H—H separation of 2.0 au for the triplet state, and no minimum is present for the singlet state.

Electron Density of Pd_6H_2 . A study of the one-electron density of a representative state of the Pd_6H_2 system may shed some additional light onto some of the results and observations of previous sections. Figure 10 shows the total oneelectron density^{**} of the ${}^{1}A_{1g}$ Pd_6H_2 system with the hydrogen atoms aligned in the (100) direction. The hydrogens are separated by 1.7 au—the energetic minimum.

^{**}Since we have implemented pseudopotentials, the "total" electron density refers only to valence electrons. However, the absence of the core should not affect the overall appearance of the electron density.



Figure 9. Singlet and triplet electronic-state H_2 interatomic potential as a function of internuclear distance in which two lattice palladiums are dynamically distorted so as to maintain optimal PdH distance.



Figure 10. Total one-electron density of Pd_6H_2 in the ${}^{1}A_{1g}$ state with the hydrogen atoms separated by 1.7 au and oriented in the (100) direction. The positions of the hydrogen atoms and palladium atoms are denoted by hexagons and triangles, respectively. Contour levels: 0.01 to 0.20 \times 0.01, and 40 to 160 \times 40.

One sees from Figure 10 that there is a fragmentary nature to the cluster; that is, there is a shared electron density between two PdH fragments, whereas the other Pd atoms in the system appear not to share as much electron density with the HH pair.

Figure 11 shows a one-electron deformation density of the same system described in the preceding paragraph in which the density of the Pd_6 lattice and the density of two H atoms have been subtracted from the total Pd_6H_2 density. This deformation should reveal changes in the electron density brought about by

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Figure 11. Density of Pd_6H_2 minus the density of Pd_6 and two H atoms. The geometry and electronic state are described in Figure 10. Contour levels: -0.08 to -0.01×0.01 , and 0.01 to 0.05×0.01 .

 $H \cdots H$ and $Pd \cdots H$ interactions. One sees from the buildup of density between the hydrogen nuclei that this state should be conducive to a bonding situation for the HH pair. This is the case, since we are at a local energetic minimum. One also sees from Figure 11 that there is a lobe-shaped decrease of electron density near each palladium, interior to the octahedral hole. This depletion of density de-shields the palladium atom from the hydrogen nucleus and may explain why the dynamic and static lattice distortion experiments were unsuccessful.

Figure 12 shows a deformation density in which we have subtracted the electron density of the lattice and the H_2 molecule from the total electron density of Figure 10. This deformation density should indicate the effect the palladium lattice has on the bonding of the HH pair trapped in the octahedral hole—particularly with regard to the observance of any electronic screening or de-screening of the HH interaction. The depletion of density between the hydrogen atoms indicates that the palladium lattice does, in fact, *de-screen* the HH interaction. This result is consistent with our above findings that the energetics of the HH interaction has a harder barrier than does free H_2 in the presence of the palladium lattice.

5. Singlet and Triplet Electronic States of Pd_3H_2 : Finally, we look at the molecule Pd_3H_2 in which the Pd_3 moiety forms an equilateral triangle with the same palladium-to-palladium distance as in the triangular face of an octahedral hole. The hydrogens are made to approach each other on a line normal to and through the center of the triangular face.

This system models the behavior of a hydrogen approaching the (111) surface of the metal with a second hydrogen already absorbed beneath the first layer of palladium atoms. The symmetry of the system is D_{3h} .



Figure 12. Density of Pd_6H_2 minus the density of Pd_6 and H_2 . The geometry and electronic state are described in Figure 10. Contour levels: same as in Figure 11.

The lowest singlet electronic structure of the Pd_3H_2 system exhibited many similarities to the lowest singlet states of Pd_6H_2 . It was found that the occupied orbital of lowest energy was dominated by contributions from the bonding $1s_H + 1s_H$ atomic orbitals. The second lowest occupied molecular orbital was dominated by the antibonding combination of 1s orbitals centered on each hydrogen. As with Pd_6H_2 , the remaining occupied orbitals formed a band and there was a one-to-one correspondence between the symmetries of the orbitals in the band and those orbitals in the set of symmetry-adapted *d* functions centered on each of the three palladiums. The symmetry of the HOMO was a'_2 and the symmetry of the LUMO was e'. A few tenths of an electronvolt higher in energy than the LUMO resided an a'_1 virtual orbital dominated by $2s_H + 2s_H$ atomic orbital contributions. The energy of this orbital decreased with decreasing HH separation.

We investigated both the lowest singlet state and an ${}^{3}A'_{2}$ excited state that resulted from the promotion of an electron from the a'_{2} HOMO to the $2s_{H} + 2s_{H}a'_{1}$ virtual. These results are shown in Figure 13. For the singlet state, at a HH separation of 2.0 au, the HH cohesion energy is greater than for free H₂ by more than one electronvolt. Even the ${}^{3}A'_{2}$ excited state has a slightly positive value of the cohesion energy at large HH separation. Once again, though, at short distance, the interatomic potential indicates a longer classical turning point for the HH interaction than in free H₂.

III. Summary and Discussion

We have investigated the electronic structure of palladium-hydrogen systems. Our investigation, guided in part by chemical intuition, included a variety of sin-



Figure 13. Intermolecular potential for the ${}^{1}A'_{1}$ and ${}^{3}A'_{2}$ excited states for Pd₃H₂ as a function of HH separation.

glet and triplet electronic states of neutrals, with and without lattice deformations. We found no systems that gave an enhanced attractive hydrogen-hydrogen interatomic potential. For the arrangement of two hydrogens occupying the same octahedral hole, it appears that the hypothesis that the electron density from the palladium lattice might screen the HH interaction is unlikely. This study suggests the opposite—namely, the palladium—hydrogen bonding interactions in the octahedral hole results in a buildup of electron density between the palladium and hydrogen atoms and a subsequent depletion of density between hydrogens. As we have seen, this de-screening of the HH interaction results in an interatomic potential with a "harder" repulsive wall.

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