Cold Fusion: How Close Can Deuterium Atoms Come inside Palladium?

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We use *ab initio* density-functional calculations to determine the structural and electronic properties of deuterium in bulk palladium. The focus of our study is the binding and the nearest-neighbor distance between D atoms in the very concentrated limit of a hypothetical PdD_2 crystal. These results are compared to analogous calculations for bulk PdD and Pd. We find that even at very high D concentrations in the bulk, the equilibrium distance between two D atoms is increased by ≈ 0.2 Å from the gas value of 0.74 Å. This large internuclear distance makes a cold-fusion reaction of deuterium very improbable.

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Large-scale utilization of the nuclear fusion of deuterium as a major energy source has so far been limited by technological difficulties to confine D atoms at appropriate densities and temperatures for a sufficiently long time. It is not surprising that attempts have been made to find an appropriate "catalyst" to ease this reaction. The earliest reports dating from the 1920's claim having detected the reaction from hydrogen to helium in Pd crystals using standard techniques of chemical analysis.[1] Very recently, the attention of the world public has been caught by reports of the observation of neutrons[2,3] and heat[3] from deuterium-loaded palladium metal.

Since the deuterium fusion reaction is induced by quantum-mechanical tunneling, its probability depends crucially on the nearest-neighbor distance between D atoms. Recent calculations[4,5] have shown that in order to explain reaction rates consistent with the observations of Refs. 2 and 3, distances between D atoms must be strongly reduced with respect to the equilibrium distance of D_2 of 0.74 Å. The key question in the discussion of cold fusion is whether this large interatomic separation of D is strongly reduced within the stable matrix of metals such as palladium.

In order to answer this question, we calculate the interactions between D atoms and bulk Pd in the high-concentration limit using a first-principles total-energy calculation within the local-density approximation (LDA).[6] Since the total energy is independent of the isotope mass for frozen atomic positions, our results for the Pd-D and Pd-H system are the same.

There is ample information available about hydrogen in metals in general[7] and both experimental[8,9] and theoretical[10] information about the Pd-H system in particular. Pd easily forms the compound PdH, where each octahedral site of the fcc-Pd structure is occupied by one H atom[8] and where the lattice constant expands by 6%.[9] The nearest-neighbor separation between hydrogen atoms in PdH is 2.9 Å. It is clear that H atoms can only get closer together in regions of the crystal where the local hydrogen concentration exceeds that of PdH. The probable absorption site in a hypothetical crystal PdH_2 might still be an octahedral site since it can easily accommodate an H_2 molecule within the billiard-ball model (using $r_{Pd}=1.38$ Å and $r_H=0.37$ Å). The H_2 bond length is smallest if the molecular axis is aligned with the octahedron axis (inset in Fig. 1) and is likely to expand if this condition is relaxed.

We calculate the total energy using the *ab initio* pseudopotential local orbital method which has been described elsewhere[11] and successfully applied to bulk transition metals and hydrogen adsorption on Pd surfaces.[12] In our calculation, we replace ionic potentials by norm-conserving ionic pseudopotentials of the Hamann-Schlüter-Chiang type.[13] We use the Hedin-Ludqvist[14] form of the exchange-correlation potential. The LDA calculations are carried out using a basis of Gaussian orbitals which are localized on atomic sites. At each Pd site, we consider *s*, *p*, and *d* orbitals with four radial

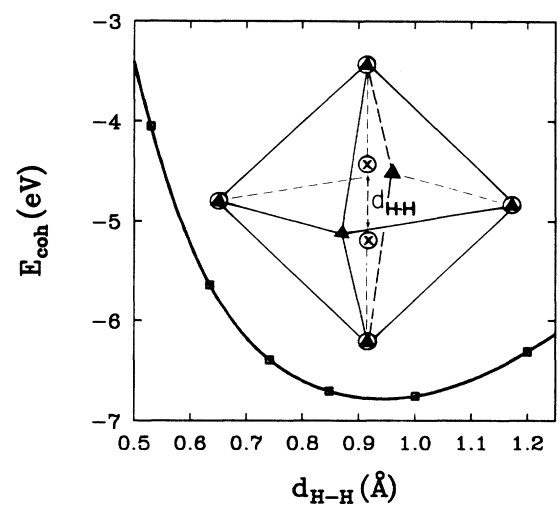

FIG. 1. Cohesive energy E_{coh} of PdH_2 as a function of the nearest-neighbor H-H separation $d_{H\text{-}H}$ in bulk palladium. The calculated points are shown by squares. Inset: The octahedron cage geometry, with the Pd atoms given by black triangles and the H atoms by crosses.

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Gausian decays each; i.e., forty independent basis functions. For hydrogen sites, we use sixteen basis functions of s and p type. We use an energy cutoff of 64 Ry in the Fourier expansion of the charge density in order to ensure complete convergence of the LDA spectrum and total energies. The LDA charge density and potentials have been obtained by sampling the Brillouin zone with a fine mesh of 1331 k points for bulk PdH and Pd and 250 k points for PdH_2, using a special-point scheme.[15] The computations of PdH_2 turned out to be more demanding due to the substantially reduced symmetry of PdH_2 as compared to bulk PdH or Pd.

In Fig. 1 we present the calculated cohesive energy of PdH_2 as a function of the H_2 bond length $d(H_2)$. We assumed that the lattice constant of the Pd structure is expanded by 6% in agreement with our calculations[16] for PdH and the experiment.[8] We define the cohesive energy of PdH_n with respect to *isolated* atoms by

$$E_{\rm coh}({\rm PdH}_n) = E_{\rm total}({\rm PdH}_n) - E_{\rm total}^{\rm atom}({\rm Pd}) - nE_{\rm total}^{\rm atom}({\rm H})$$

and find for PdH $E_{\rm coh}({\rm PdH}) = -6.28$ eV which compares favorably with the experimental value[17] $E_{\rm coh}^{\rm expt}({\rm PdH}) = -6.65$ eV. Stability of the corresponding crystals can be investigated best by comparing formation energies of PdH_n (starting from *bulk* palladium and *molecular* hydrogen) which is given by

$$E_{\rm form}({\rm PdH}_n) = E_{\rm total}({\rm PdH}_n) - E_{\rm total}({\rm Pd\ bulk}) - \tfrac{1}{2}nE_{\rm total}({\rm H_2\ molecule}).$$

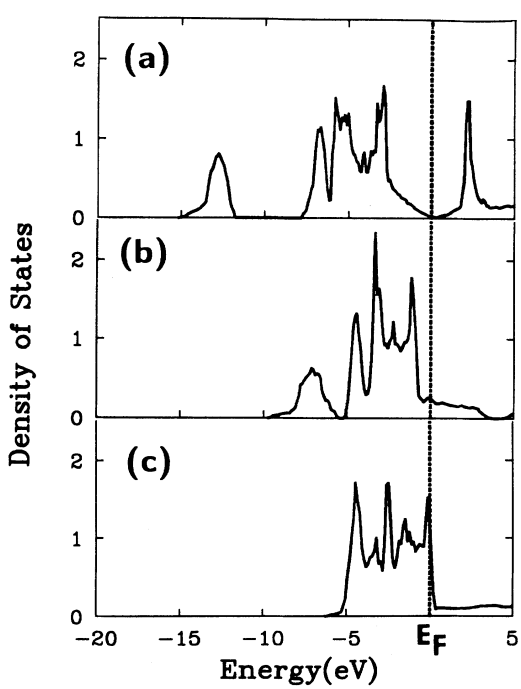

FIG. 2. Calculated total density of states $N(E)$ of (a) PdH_2 ($d_{\rm H\text{-}H}$=0.74 Å), (b) PdH, and (c) Pd.

This definition yields $E_{\rm form}({\rm PdH}) = -0.53$ eV and $E_{\rm form}({\rm PdH_2}) = +1.34$ eV indicating a compound-forming tendency of PdH and structural instability of PdH_2, again in agreement with experiment.

$E_{\rm coh}$ is related to the H-H interaction potential which is strongly anharmonic as suggested by our results in Fig. 1. Our results show that the intramolecular distance $d(H_2)$ is *expanded* to 0.94 Å in the Pd lattice even at very high H concentrations in the hypothetical crystal PdH_2. At this large distance, cold nuclear fusion is even less probable than in the deuterium gas phase.[4]

The origin of the large distance between hydrogen atoms in bulk Pd can be understood from the density of states and the charge density of the Pd-H system. In Fig. 2 we compare the total density of states of PdH_2 to that of PdH (at the same volume) and to bulk Pd at its equilibrium volume. In agreement with previous calculations for PdH in the bulk phase[10] and for the surface adsorption[12] of H/Pd(001), we find that the binding between H and Pd is predominantly covalent, giving rise to a bonding split-off state at ≈ -13 eV (with respect to E_F) in PdH_2 [Fig. 2(a)] and at ≈ -8 eV in PdH [Fig. 2(b)]. To a lesser extent, hybridization with hydrogen also modifies the $4d$ density of states of Pd by changing its form and pushing the center of gravity towards higher

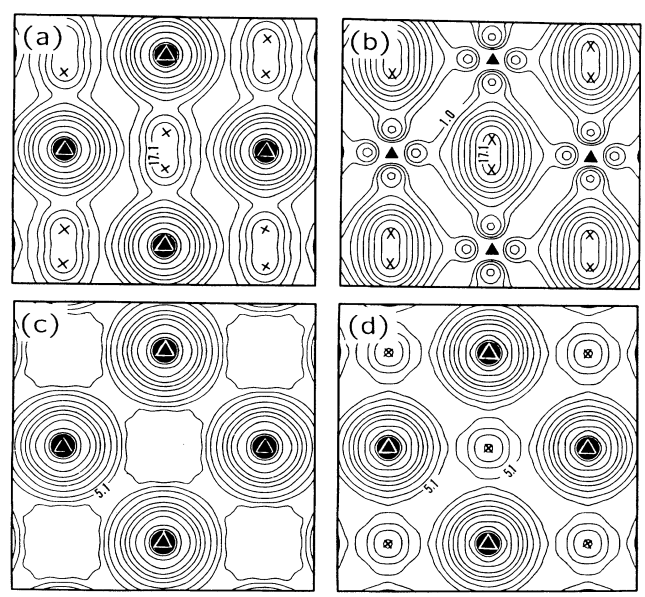

FIG. 3. (a) Calculated charge density $\rho(\mathbf{r})$ and (b) charge density corresponding to the hydrogen-induced split-off states [at $E \approx -13$ eV in Fig. 2(a)] of PdH_2 ($d_{\rm H\text{-}H}$=0.74 Å). Total charge density (c) of bulk Pd and (d) of bulk PdH. All contour plots are shown in the (100) plane which contains circled Pd and H atoms in the inset in Fig. 1. The position of Pd atoms is marked by black triangles; that of H atoms by crosses. The charge density is in units of 10^{-2} electron/a.u.^{3}; the ratio of two consecutive contours is $\rho(n+1)/\rho(n) = 1.5$.

binding energies for increasing H concentration. This means not only an increased filling of the $4d$ band causing loss of cohesion, but also transition to a semimetal in the extreme case of PdH_2

In Fig. 3 we compare total charge densities of PdH_2, PdH, and bulk Pd. As mentioned earlier, the H_2 molecule fits easily into the Pd octahedral cage [Fig. 3(a)] and fills the low-charge-density region inside [Fig. 3(c)]. Even at a H-H distance of 0.74 Å, the separation between H and Pd atoms is close to 1.7 Å which is a typical molecular bond length. No large values of the charge density can be found in the Pd-H system which would make this bonding geometry energetically unfavorable. For comparison, we show the total charge density of PdH in Fig. 3(d). Because of the small size of the H atom, the interaction potential with the surrounding Pd matrix is very shallow, which gives rise to very low vibration frequencies for the similar adsorption site at the surface.[12] From the charge-density difference we conclude that there is a small net charge transfer from Pd to H (typically <0.5 electron near the equilibrium distance).

Finally, in order to understand the interaction of H with Pd in the high-concentration limit, we investigated the character of the split-off bonding states in PdH_2. The corresponding charge density, which is given in Fig. 3(b), shows that the bonding state arises from the interaction between the H $1s$ and Pd $4d$ orbitals. From a direct comparison with the total charge density given in Fig. 3(a) we find that this state contains nearly all of the electrons residing on H. This rehybridization of H_2 orbitals leads to an increase of the intramolecular bond length since the H_2 bond charge is being depleted and since the H bonding electrons are partly shared with Pd in the case of PdH_2.

In conclusion, we calculated the interaction of deuterium (or hydrogen) with Pd metal in the case of a hypothetical crystal PdH_2 and bulk PdH in the framework of the *ab initio* density-functional formalism. We found that even at very high D concentrations in the bulk, the equilibrium distance between two D atoms is increased by ≈ 0.2 Å from the gas value of 0.74 Å. This bond length increase has been traced back to the formation of a covalent bond between H atoms and Pd atoms in the surrounding octahedron cage. This large nearest-neighbor distance between D (or H) atoms makes a cold-fusion reaction of deuterium very improbable.

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[17]$E_{\rm coh}^{\rm expt}(\rm PdH) = -6.65$ eV can be obtained from a thermodynamic cycle as a sum of the formation energy of PdH (from bulk Pd and atomic H), -2.76 eV per H atom, and the bulk cohesive energy of Pd, -3.89 eV per atom.