Instability of Diatomic Deuterium in fcc Palladium

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To clarify some of the solid-state aspects of cold fusion in deuterated transition metal electrodes, we have carried out first-principles self-consistent total energy calculations for various configurations of atomic and diatomic deuterium inside fcc palladium. We find that the stability of the Pd + D system is controlled by the relative position of the deuterium-induced antibonding level with respect to the Fermi energy. The equilibrium D-D distance in dense PdD\(_\alpha\) up to \(\alpha = 3\) is found to be much larger than the free space value. The calculated Born-Oppenheimer energy surface of diatomic D\(_2\) in crystalline palladium is shown to have but metastable local minima whose internuclear separation is at least 0.2 Å larger than that of the isolated D\(_2\) molecule. We conclude that D\(_2\) in crystalline Pd will have a substantially lower tunneling probability than hitherto thought and that explanation for fusion mechanisms should be sought elsewhere.

Recent suggestions of room-temperature ("cold") nuclear fusion in deuterated transition metal electrodes\(^1,2\) have raised interest in the physics of dense deuterium atoms in the field of transition metals. Of recent interest here is the Born–Oppenheimer energy surface \(E(R)\) of two deuterium atoms at a distance \(R\), since both the vibrational wavefunction \(\psi(R)\) of diatomic deuterium [determining the fusion rate\(^3\) \(A = A|\psi(R=0)|^2\)] and the tunneling barrier penetration factor\(^3\) \(B\) depend sensitively on \(E(R)\). Previous estimates\(^3\) of \(A\) and \(B\) assumed the free space form\(^4\) of \(E(R)\) of gaseous H\(_2\) [bound at \(R_{eq} = 0.74\) Å by \(E(R_{eq}) = 4.7\) eV/2H; since \(E(R)\) is independent of the isotope mass effects, the discussion below applies equally to H and D]. Because the equilibrium distance \(R_{eq}\) for the isolated H\(_2\) molecule is too large to grant sufficient tunneling events\(^3\), various solid-state \(R_{eq}\)-shortening mechanisms were sought. It was hoped, for example, that the existence of a metal lattice (e.g., fcc Pd) in which deuterium is embedded could grant a large Coulomb screening effect and, hence, substantially reduce the D–D tunneling distance and enhance the fusion rate.

In an attempt to clarify some of the solid-state aspects of cold fusion,\(^1,2\) we have used first-principles self-consistent total energy methods within the local density formalism\(^5\) to predict systematically the stability of various periodic arrangements of atomic and diatomic hydrogen in fcc palladium. This approach, implemented within the all-electron full-potential semirelativistic linearized augmented plane wave (LAPW) method,\(^6\) includes interelectronic Coulomb and exchange-correlation interactions and provides an accurate solution to the electronic Schrödinger problem for a static periodic atomic configuration \(\{R\}\) of the combined Pd + H system. We study various orientations of H\(_2\) in fcc Pd, finding that [111] is the stablest; a molecule in any other orientation will spontaneously reorient along [111]. However, we find that in this orientation the system can further lower its energy by dissociating into two H atoms each at a tetrahedral interstitial site, leading thereby to a yet longer H–H separation. Subsequent penetration of the diffusion barriers (−0.3 eV) leads, then, to an exothermic hopping into the octahedral sites. Bringing two such octahedrally

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positioned H atoms to the equilibrium internuclear separation of an isolated H₂ molecule requires investment of 2.4 eV/2H; the same reaction in the gas phase emits 4.7 eV/2H.

In the present study we have used 10 special k-points for Brillouin zone integrations in the fcc structure and their equivalent points for the other structures. Large basis sets (-170 basis functions per Pd atom, corresponding to a kinetic energy cutoff of 21 Ry) and correspondingly large sets of potential and charge density components (Ecutoff = 204 Ry) are used. The formation enthalpy per H atom of a Pd-H structure with a hydrogen-to-palladium atom ratio α = H/Pd is defined as

\[ \Delta H_{\text{PdH}_\alpha} = \frac{1}{\alpha} E_{\text{PdH}_\alpha} - \frac{1}{\alpha} E_{\text{Pd}_\alpha} - \frac{1}{2} E_{\text{H}_2\alpha} \]

(1)

In the absence of competing reactions, negative (positive) \( \Delta H \) denotes thermodynamic stability (instability) toward disproportionation into metallic Pd and gaseous H₂.

Pure Constituents. We first establish the reference total energies of solid (s) fcc Pd and gaseous (g) H₂. For pure fcc Pd we find an equilibrium lattice constant \( a_\text{eq} = 3.85 \) Å and a cohesive energy of \( E_c = 5.05 \) eV (3.95 eV if treated nonrelativistically). The binding energy curve for the free H₂ molecule is calculated in a simple cubic supercell geometry with lattice constant \( a = 4.00 \) Å, where H₂ is centered at the cubic site. This gives a molecular dissociation energy of 4.73 eV/pair at the calculated equilibrium internuclear distance of 0.769 Å; the vibrational energy is \( \hbar \omega = 0.54 \) eV, all in reasonable accord with experiment and previous calculations.\(^8\)

Our results for the relative energies of various PdH_{\alpha} structures are depicted graphically in Fig. 1, where two reference energies are shown for convenience.

Dilute H in Pd. We model the small-\( \alpha \) (dilute) limit by placing an H atom at the octahedral (O) center of an fcc Pd cubit unit cell (\( \alpha = 0.25 \), Pd₄H, denoted as SC in Fig. 1). The calculated octahedral formation enthalpy \( \Delta H_{\text{O}} = -0.28 \) eV/H is exothermic; it is in fair agreement with the observed formation enthalpy of \( -0.14 \) to \( -0.16 \) eV/H. Examination of the electronic structure in this dilute limit reveals a simple physical picture, consistent with previous studies;\(^10\)-\(^12\) the attractive potential of H⁺ pulls to lower energy those Pd wavefunctions which have an \( \alpha \) symmetry about the octahedral site (the "interstitial insertion rule"),\(^13\) forming bonding H--Pd states near the bottom of the valence band, centered at \( E_F - 7.9 \) eV. This lowering of the energy of the states of pure Pd stabilizes the system. On the other hand, the small volume expansion (calculated to be \( \Delta V = -1.7 \) cm³/g-atom of H for \( \alpha < 1 \)) and the lowering of the H-induced antibonding states with respect to the Fermi energy \( E_F \) both destabilize the system. The balance is attractive for low \( \alpha \) because the antibonding states are essentially unoccupied. Dilute hydrogen in Pd is found to be over-screened by the Pd electrons relative to atomic hydrogen, forming a negative ion "H⁻". Despite this, the nearest-neighbor H--H distance (> 2.75 Å) is considerably larger than for the covalent free-space molecule.

Higher \( \alpha \)'s and Ordered Phases. In the fcc structure each Pd [with Pd at the (0,0,0) position] has two tetrahedral (T) interstitial sites [at (1/4,1/4,1/4) and (3/4,3/4,3/4)] and a single octahedral (O) interstitial site [at (1/2,1/2,1/2)], all empty in pure Pd. Partial or full occupation of these sites by H leads to a number of possible ordered phases. For \( \alpha = 0.5 \) we can occupy, in an ordered fashion, half of the O sites by hydrogen, forming the observed low-temperature tetragonal \( \gamma \)-phase Pd₃H₂ of space group \( I4_1/amd \), or \( D_{19}^9 \). Alternatively, one can

![Fig. 1. Calculated formation enthalpies \( \Delta H(\text{PdH}_\alpha) \) with respect to Pd and \( 1/2 \) H₂(g) or Pd(s) + H(g). Filled circles, stable phases; open circles, unstable phases. See text for notation of crystal structures. The results for \( \alpha = 0.5 \) (except the \( \gamma \) phase) are calculated at fixed lattice constant (\( a = 4.00 \) Å); others are calculated at their respective equilibrium values.](image-url)
occupy both tetrahedral sites along the [111] direction, forming the “T + T structure” of Pd₄H₂, also with α = 0.5. For α = 1, we can either occupy the O site to form the NaCl structure of PdH or occupy one of the T sites, to form the ZnS structure of PdH. For α = 2, it is possible to occupy all the T sites, forming the CaF₂ structure, or occupy T and one O site to form the LiAlSi-like structure of PdH₃. Finally, for α = 3, occupation of all three interstitial holes (2T + O) forms the BiF₃ structure of PdH₃ (see Ref. 15 for further description of these crystal structures). We calculated the formation energies of all of these structures; Fig. 1 shows the results. We find the following.

(i) ΔH is negative for all but the LiAlSi and BiF₃ structures of PdH₂ and PdH₃, respectively; if formed, these two compounds would disproportionate, releasing their ΔF's thermally, as recently suggested.

(ii) ΔH₄ < 0 is a necessary but not a sufficient condition to imply local stability of structure α. For example, the CaF₂ structure of PdH₂ has a higher ΔH than PdH + 1/2H₂(g) (a point denoted by an asterisk on the dashed tie-line); hence, despite its ΔH₄ < 0, if formed, it, too, will decompose into these components, releasing the corresponding heat.

(iii) For α ≤ 1, the system shows preference for occupation of O over T, since T has a shorter Pd-H distance (\( \sqrt{3} a/4 \)) relative to that for O: (a/2). On the other hand, for larger α (e.g., α = 2), we find that the system prefers occupation of two T sites over occupation of O + T, since the H–H distance is longer in the latter case, leading to a stronger H–H repulsion. This is consistent with experimental observations.

(iv) Hydrogen occupation of the T site is accompanied by a large lattice relaxation. Indeed, the calculated lattice constant for PdH in the zincblende structure (4.17 Å) is about 0.11 Å larger than that for PdH in NaCl structure. In a rigid lattice, the T-site formation enthalpy ΔH₄ is 0.23 eV higher than the O-site value. Allowing for lattice relaxation lowers this value to 0.13 eV.

(v) The diffusion path between the O and T sites passes through a barrier located near the (\( 1/4, 1/4, 1/4 \)) position. The rather small barrier value we find (-0.3 eV) is consistent with the rapid diffusion of H in Pd.

The pertinent physics here is that as α increases from the dilute limit, the coupling between the H and the Pd atoms lowers the hydrogen-induced H–Pd bonding states, thereby stabilizing the system. However, further increase in α lowers the hydrogen-induced antibonding states below the Fermi energy, causing destabilization. The H-induced lattice dilation of the host also contribute to destabilization. This self-limiting process controls the maximum amount of incorporable hydrogen at equilibrium.

Our study indicates that the equilibrium H–H distance in PdHₐ up to α = 3 (> 1.73 Å) is much larger than the free-space value, despite that H is effectively screened in fcc Pd.

Diatomic H₂ in Pd. We next inquire whether there exists a metastable phase of H₂ dimer in Pd with a smaller \( R_{eq} \) than the free-space value. We model this system at \( \alpha = 0.5 \) by an octahedrally centered H₂ molecule inside an fcc cube with interatomic separation \( R \) and orientation \( \overrightarrow{G} \). Varying \( R \) at \( a_{eq} = 4.00 \) Å (close to the calculated equilibrium lattice constant) for the orientations \( \overrightarrow{G} = [111], [001], \) and \([110]\), we find the Born–Oppenheimer energy curves \( E[\alpha_{eq}, \overrightarrow{G}, R] \) shown in Fig. 2. The basic results are as follows.

(i) Octahedrally centered diatomic H₂, kept at its gas-phase internuclear separation \( R_{eq}[H₂(g)] \), is unstable by as much as -1.5 eV with respect to disproportionation into Pd⁹ + H₂ for all principal orientations (Figs. 1 and 2).

![Fig. 2](image-url)
(ii) A few local minima exist in the energy surface, corresponding to metastable molecules. However, all are characterized by H–H internuclear separations at least 0.2 Å larger than the free-space value (denoted as “gas-phase eq. dist” in Fig. 2).

(iii) The H₂ is stabilities in the [111] orientation. A molecule in any other orientation would spontaneously reorient to [111].

(iv) At this position, the molecule will spontaneously dissociate into two isolated T sites (separated by a distance $\sqrt{3}a/2 = 3.5 \text{ Å}$, see Fig. 2), thereby lowering the energy to the value $2\Delta H_T = -0.44 \text{ eV}/2\text{H} (-0.54 \text{ eV} \text{ if the host lattice is relaxed}).$ Subsequently, these atoms could penetrate the O–T diffusion barrier and relax to the O sites, releasing $2\Delta H_T - 2\Delta H_O = 0.36 \text{ eV}/2\text{H}$ (see Fig. 1). Hence, while bringing two hydrogen atoms together in free space to $R_{eq} [H_2^{(g)}]$ emits $-4.7 \text{ eV}/2\text{H}$, bringing two octahedrally dissolved H's to the same distance in Pd requires investment of $-2.4 \text{ eV}/2\text{H}.$

We identify the electronic origins of the instability of H₂ in Pd as follows: dissolving small amounts of H in Pd stabilizes the system principally because the energy lowering associated with the formation of deep Pd–H bonding states near the bottom of the valence band overwhelms the energy increase associated with volume expansion and with a slight lowering of the yet empty antibonding states. On bringing closer together two initially isolated and screened H atoms inside Pd, the stable Pd–H bonding state is gradually destroyed and replaced by the weaker H–H interaction, which forms a bonding (“$\Sigma_{1g}$”) and an antibonding (“$\Sigma_{1u}$”) state.$^{19}$ The H–H bonding state lies at about 13 eV below $E_g$ and is separated from the antibonding state by a “molecular gap” $E_g.$ In the free molecule, $E_g$ is $\sim 10 \text{ eV}.$ In the Pd host, where the odd (u) and even (g) state are screened by Pd valence electron, the gap $E_g$ is even smaller. The significant point here is that this molecular gap is smaller than the Fermi energy, hence even the antibonding H–H state is occupied. This is the principal reason for the system’s instability at high hydrogen content and for the formation of the H₂ molecule: the molecule seeks to dissociate to avoid population of its antibonding state. It is this electronic mechanism (not the internuclear repulsion which is effectively screened for H₂ inside Pd) which is the origin of the instability of the embedded molecule.

Clearly, none of the equilibrium structures shown in Figs. 1 and 2 are conducive to cold fusion, since the equilibrium H–H distance in Pd is considerably larger than that of the free molecule (Fig. 2). Equilibrium fusion rates must be enormously smaller than what was previously$^3$ thought. Use$^{5,4}$ of free H₂ potential to estimate fusion probabilities inside Pd would seem unreasonable. We conclude that there are no spectacular solid–state effects (e.g., enhanced effective masses) in crystalline transition metal which would significantly reduce $R_{eq}.$ Search for such effects should perhaps be sought in noncrystalline environments (e.g., defects, grain boundaries).

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REFERENCES