

Editor's Comments: This paper carefully explores a possible source of excess heat in certain types of electrochemical cells. As this effect is chemical, not nuclear, the occurrence of excess heat together with "nuclear byproduct" would be a confirmation of the occurrence of nuclear reactions. The cold fusion experimenter should be aware of the effect that the latent heat of water can have on his/her experiments. Because many papers have reported both excess heat and nuclear byproducts, this paper is not the full explanation of excess heat generation, but it is certainly an excellent contribution to the understanding of the complex phenomena that we have labeled "cold fusion."

**JAHN-TELLER SYMMETRY BREAKING
AND HYDROGEN ENERGY IN γ -PdD "COLD FUSION"
AS STORAGE OF THE LATENT HEAT OF WATER**

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ABSTRACT

In 1989, we proposed a common quantum-chemical basis for superconductivity and anomalous electrochemical properties of palladium loaded with hydrogen and deuterium, derived from H-H/D-D bonding molecular orbitals at the Fermi energy between tetrahedral interstices (" γ -phase" PdD). Symmetry-breaking anharmonic vibrations of the protons/deuterons, induced by the dynamic Jahn-Teller effect, promote superconductivity in PdH/PdD at $T_c = 9/10^\circ\text{K}$, while the large vibronic anharmonicity explains the inverse H/D isotope shift of T_c . The calculated deuteron vibronic amplitude of 0.46\AA implies a closest D-D approach of 0.76\AA between neighboring tetrahedral sites and fusion rate of only $\sim 10^{-24}$ per deuteron pair per second in γ -PdD at ambient temperature, much too small to explain reported excess heats. *Ab initio* quantum-chemical computations for γ -PdD further indicate that the "channels" connecting tetrahedral sites provide, via the Jahn-Teller effect, an "orbital pathway" for bulk catalytic recombination of atomic deuterium to rapidly diffusing dideuterium, $4\text{D} \rightarrow 2\text{D}_2$, the recombination heat equaling 9.4eV per Pd atom per unit diffusion cycle time, equivalent to the storage and release of latent vaporization heat of 2.5 moles of D_2O . While the diffusion cycle time depends on cell conditions, for cycles between 1 and 100 minutes, this process could generate 17 to 1700 watts/cm³ of stored latent heat in γ -PdD. The inverse isotope effect implies a slower hydrogen reaction, $4\text{H} \rightarrow 2\text{H}_2$, and diffusion in γ -PdH, leading to negligible latent heat power from Pd-based light-water cells. However, this mechanism could explain reported heat generation in light-water cells using nickel cathodes, where $2\text{H} \rightarrow \text{H}_2$ catalysis is a rapid (110) surface or near-surface phenomenon.

The Dynamic Jahn-Teller Effect, Superconductivity, and D-D Fusion

An abstract theorem proposed in 1936 by Jahn and Teller^[1] laid the foundation for a theory of the static and dynamic coupling of nuclear motions to electronic structure. In a 1983 paper^[2] on a "real-space" molecular-orbital basis for superconductivity, we first suggested that Cooper pairing and the inverse isotope shift, $T_c = 9/10^\circ\text{K}$, in PdH/PdD are associated with dynamic Jahn-Teller-induced *anharmonic* vibrations of the protons/deuterons inside Pd. The amplitudes of these vibrations are determined from the formula [2]:

$$\delta = (m/M)^\beta d \tag{1}$$

where M is the atomic mass, m is the conduction electron mass, d is the interatomic distance, and $0 < \beta \leq 1/2$ is the anharmonicity. In the "harmonic limit, $\beta = 1/2$, the dynamic Jahn-Teller-induced vibrations reduce to the "virtual phonons" of the BCS theory of superconductivity. In Ref. 2 it was shown how β follows directly from the bond overlap of degenerate molecular orbitals at the Fermi energy (E_F). This theory has since been successfully applied to high- T_c oxide and fullerene superconductors.^[3,4]

In more recent work,^[5] we have confirmed, from density-functional molecular-orbital and *ab-initio* Hartree-Fock calculations, that for high H/D loading in palladium, the sole occupation of octahedral interstices is Jahn-Teller unstable toward migration of H/D's to the tetrahedral interstices, forming the so-called " γ -phase" of PdH/PdD. Spatially extended, degenerate H-H/D-D bonding molecular orbitals at E_F between the tetrahedral sites in γ -PdH/PdD are found to be a precursor to Cooper pairing, superconductivity at $T_c = 9/10^\circ\text{K}$, and the inverse isotope effect on T_c . The hydrogen molecular orbitals at and just above E_f are σ -bonding along and σ -antibonding in "channels" of opposite phase $\psi +$, ψ - connecting tetrahedral interstices, as shown schematically for γ -Pd in Fig. 1 and computationally in Fig. 2 as a contour map through a (110) plane. D-D σ -bond overlap is enhanced by the "compression" effect of significant Pd(4d)-D(1s) antibonding at E_F (Fig. 2). Indeed Pd(4d)-D(1s) antibonding at E_F substantially weakens the effect of Pd(4d)-D(1s) bonding states below the Pd d-band, explaining the small heats of formation of PdD, while promoting delocalized D-D σ -bonding molecular orbitals at E_F . Evidence for hydrogen atoms "banding" together on nickel (110) surfaces, with electron density similar to that shown in Fig. 1, has recently been reported.^[6]

In the dynamic Jahn-Teller coupling between interstitial D-D σ -bonding electrons at E_F and anharmonically vibrating deuterons required for Cooper pairing and superconductivity in PdD for $T_c \leq 10^\circ\text{K}$, there is continual symmetry-breaking dynamical interconversion between alternate D-D σ -bond deformations, δ , along the three crystallographical equivalent directions of the "bonding channels" $\psi+$ and $\psi-$ shown in Fig. 1 and Fig. 2. These rapid oscillations of the deuterons are equivalent to "anharmonic local optical phonons" of amplitude δ given in Equation (1). For the calculated D-D bond overlap between tetrahedral sites in γ -PdD (Fig. 2), $\delta = 0.46\text{\AA}$.

Under the influence of the Jahn-Teller effect, the D-D nuclear fusion rate can be calculated from the formula:^[5]

$$R = (\hbar\sigma / M\delta^3 d^4) \exp\left[-(2/\hbar)(d-2\delta)\sqrt{2M(V-\hbar^2/2M\delta^2)}\right] \quad (2)$$

where σ is the fusion cross-section extrapolated to ambient temperature and V is the Coulomb potential barrier between the γ -PdD tetrahedral sites (" T -sites") and the " S -sites" half way between neighboring T -sites along the D-D bond direction (Fig. 2). Combining formulas (1) and (2) and using the relationship between anharmonicity, β and bond overlap,^[2,5] R can be plotted as a function of D-D bond overlap, leading to the graph of Fig. 3. For the 20% D-D overlap characteristic of γ -PdD (Fig. 2), this graph gives a value of $R = R_0 \cong 10^{-24}$ fusion per deuteron pair per second, resulting from the Jahn-Teller effect. This value is of the same order of magnitude as that determined from neutron counts in electrochemical experiments on deuterated electrodes by Jones *et al.*^[7] Clearly, this very low level of fusion, while fifty orders of magnitude larger than that expected for an isolated D_2 molecule, is not large enough to produce significant amounts of heat under electrochemical conditions in PdD.

It is theoretically possible to enhance the effective D-D bond overlap in γ -PdD to almost 33% via alloying (see below), increasing the D-D fusion rate to a maximum of $R \cong 10^{-21}$ according to Fig. 3, but still too

small for significant heat production.

Symmetry Breaking, D-D Recombination, and Hydrogen Energy in PdD

The D-D potential energy surface in γ -PdD, calculated from *ab initio* Hartree-Fock theory, resembles the "Mexican hat" shown in Fig. 4. The high-symmetry (T_d) coordination of a Pd atom by four D atoms in four of the eight surrounding face-centered-cubic Pd tetrahedral interstitial sites is Jahn-Teller unstable, leading to a central energy minimum of distorted tetrahedral (C_{3v}) symmetry at the "crown of the hat" and a square coplanar (D_{2h}) "broken-symmetry" energy minimum at the "brim of the hat," 9.4eV below T_d symmetry, for an equilibrium D-D distance of 0.76Å. The latter is practically equal to the equilibrium bond distance of a free D_2 molecule. The 9.4eV energy per Pd atom released in the Jahn-Teller distortion of each PdD_4 molecular unit in γ -PdD from T_d to D_{2h} symmetry is likewise remarkably close to the sum of the chemical bond energies of two free D_2 molecules.

Thus, the D-D "bonding channels" connecting tetrahedral sites in γ -PdD provide, via the symmetry-breaking Jahn-Teller effect, an "orbital pathway" for the bulk catalytic recombination, $4D \rightarrow 2D_2$, of rapidly diffusing atomic deuterium to rapidly diffusing dideuterium, the large exothermic chemical heat of recombination equaling 9.4eV per Pd atom. Once a steady state of high electrochemical loading is achieved, this process is likely to be rapid and continuous, facilitated by the Jahn-Teller displacement of diffusing atomic deuterium from octahedral to tetrahedral interstices, forming the " γ -phase," then rapidly diffusing as dideuterium through the γ -PdD "bonding channels" connecting the tetrahedral sites to the cathode surface, where the dideuterium escapes as D_2 gas.

It is impractical to calculate a precise cycle time for this process, because the diffusion depends on the input electrical current, the ambient temperature and pressure, the structural integrity of the Pd lattice, and the surface condition of the Pd cathode. However, if the cycle time for recombination, $4D \rightarrow 2D_2$, is somewhere between 1 and 100 minutes, at 9.4eV per Pd atom per unit time, this process could generate heat at a rate of 17 to 1700 watts/cm³ palladium. For this power range, the total heat released over ten minutes would be between 10KJ and 1MJ. This is consistent with the wide range of "excess" powers reported in laboratories around the world.

"Cold Fusion" Heat as Chemical "Latent Heat"; "Heat after Death"

This dynamical Jahn-Teller-induced catalytic mechanism is, of course, a chemical process, although an unusual one in that it corresponds to an internal phase change of the deuterium within γ -PdD. Since the energy release is effectively due to an internal cyclic γ -phase change of atomic deuterium to dideuterium, the heat produced may be viewed as "latent heat" produced by repeated formation of the "interstitial sublattice" of D-D bonds between the tetrahedral interstices in γ -PdD, as atomic deuterium diffuses into palladium and dideuterium diffuses out. "Latent heat" of 9.4eV per Pd atom for 6.8×10^{22} Pd atoms/cm³ adds up to 102KJ/cm³ palladium. Since the latent heat of vaporization of D_2O is 41.5KJ/mole at 100°C, the "latent heat" of 102KJ produced in one cm³ of γ -PdD per unit diffusion cycle time is equal to the latent vaporization heat of 2.5 moles of D_2O . In other words, the heat of "cold fusion" appears to be the storage and release of the latent vaporization heat of heavy water. Indeed, if the electric power input is turned off a fully loaded cell, this stored latent heat is sufficient to boil away 2.5 moles of D_2O , the so-called "heat after death" of Pons and Fleischmann.^[8]

Equivalence of "Excess" Heat to the Latent Vaporization Heat of Water

Why then is this heat interpreted as "excess heat"? To answer this question, one must first understand the nature of the bonding between H₂O/D₂O molecules in water. It is commonly thought that the breaking of electrostatic or weakly covalent O-H or O-D "hydrogen bonds" between neighboring water molecules accounts for all the latent heat required to take water from the liquid to vapor phase. However, a recent experimental study of the interatomic structure of water at supercritical temperatures, reported in *Nature*,^[9] has revealed that breaking of nearest-neighbor O-H and O-D bond correlations in the liquid accounts for only a fraction of the latent vaporization heat. Fig. 1 of Ref. 9 reveals that second- third- and even fourth-neighbor hydrogen-hydrogen (or D-D) bond correlations persist after the nearest-neighbor O-H/O-D and H-H/D-D bonds are broken at supercritical temperatures. These longer range H-H/D-D bond correlations account for the major part of the latent vaporization heat of water.

In the electrolysis of water, only the O-H/O-D bond correlations are broken as H/D penetrates the Pd cathode and O₂ is evolved at the anode. For high loading and the formation of γ -PdD, the D-D bond correlations accounting for a major part of the latent heat of the electrolyte are effectively "stored" cooperatively between the tetrahedral sites of the γ -PdD lattice, as described above and in Fig. 2. The release of the latent heat by the Jahn-Teller-induced bulk catalytic process, $4D \rightarrow 2D_2$, per Pd atom, effectively a cooperative γ -phase transition between interstitial atomic deuterium and dideuterium, thus is interpreted as "excess" heat. Therefore, this mechanism of storage and release of the latent heat of heavy water by palladium is more appropriately viewed as a "new hydrogen energy," the terminology commonly used in Japan instead of "cold fusion."

Light Water Versus Heavy Water

Significant amounts of "excess" heat from Pd-based light-water cells are not observed, most likely because of substantially more sluggish hydrogen diffusion in γ -PdH, compared to deuterium in γ -PdD. Although the mass of D is twice that of H, this inverse isotope effect, comparable to the one discussed above for the superconducting T_c 's of PdH and PdD, is probably due to the effectively larger diffusion cross sections of H and H₂ versus those of D and D₂, resulting from the larger amplitude, δ , of dynamic Jahn-Teller-induced anharmonic vibrations for hydrogen versus deuterium, according to Eq. (1). The larger effective radii of H and H₂ in γ -PdH markedly impede hydrogen diffusion and thus lengthen the full $4H \rightarrow 2H_2$ cycle time, as compared to the rapid D and D₂ diffusion, leading to the much faster $4D \rightarrow 2D_2$ catalytic process in γ -PdD.

Nevertheless, this mechanism may explain reported heat production from nickel cathodes in light water cells, where catalytic hydrogen recombination, $2H \rightarrow H_2$, is mainly a rapid (110) surface or near-surface phenomenon. Nickel (110) surfaces harbor the tetrahedral interstices of the bulk crystal. While the solubility of hydrogen in nickel is much lower than in palladium, the latent heat of H-H bond formation between tetrahedral sites close to the (110) surface (the "surface γ -phase" of NiH) could yield substantial heat for high-surface-area nickel, since the diffusion path to the surface is much shorter.

Supporting Experimental Evidence for $4H \rightarrow 2H_2$ Conversion

Experimental evidence for H₂ molecular "excited states" in other transition-metal hydrides has recently been reported by Baker *et al.*^[10] from proton spin-lattice relaxation data.

A molecular analogue of the $4H \rightarrow 2H_2$ process has recently been reported by Wisniewski *et al.*^[11] in the

form of an $\text{Ir}(\text{PR}_3)_2\text{ClH}_4$ complex, in which the H ligands undergo a rapid dynamical dimerization to the dihydrogen dihydride $\text{Ir}(\text{PR}_3)_2\text{ClH}_2\text{H}_2$, as shown in Fig. 5.

The Importance of Lattice Structural Integrity in Palladium

For the γ -PdD lattice to maintain an "interstitial network" of D-D bonds (Fig. 1 and Fig. 2), formed and reformed between rapidly diffusing deuterium at high loading, the structural integrity of the material is crucial. Crack tips and grain boundaries in transition metals can be sites of rapid catalytic hydrogen recombination, which tend to cause metallic decohesion, intergranular embrittlement, and crack propagation.

Enhanced "Cold Fusion" and Superconductivity in γ -Pd_{0.75}Ag_{0.25}D

Density-functional molecular-orbital calculations have been performed for a γ -Pd_{0.75}Ag_{0.25}D alloy. Maximum hydrogen solubility near this composition has been reported by Lewis^[12]. The pertinent wavefunction contour map for this alloy, showing D-D bonding between the tetrahedral sites at E_F , is displayed in Fig. 6 and may be compared with Fig. 2 for pure γ -PdD. As a result of the increased "compression" effect of Ag(4d)-D(1s) antibonding in γ -Pd_{0.75}Ag_{0.25}D at E_F , the tetrahedral D-D bond overlap in Fig. 6 is enhanced to practically 33%, as compared with 20% in Fig. 2 for γ -PdD. From Fig. 3, this would suggest a possible increase of the D-D nuclear fusion rate from $R \approx 10^{-24}$ in γ -PdD to $R \approx 10^{-21}$ in γ -Pd_{0.75}Ag_{0.25}D, which should be detectable by increased neutron emission, provided the Pd_{0.75}Ag_{0.25} alloy can be loaded with deuterium. However, this predicted increase in fusion rate is still too small to generate significant heat on its own.

Tracking this predicted increase in D-D fusion in the Pd-Ag alloy, is the experimental fact uncovered by Stritzker^[13] that the superconducting transition temperature is raised from $T_c = 9^\circ\text{K}$ (10°K) in PdH(D) to $T_c = 15^\circ\text{K}$ in Pd_{0.75}Ag_{0.25}H. This is consistent with the dynamic Jahn-Teller anharmonic vibronic mechanism for high- T_c superconductivity discussed above and in Refs. 2-5.

"Cold Fusion" in High- T_c Superconductors

In accord with the above thesis that a dynamic Jahn-Teller anharmonic vibronic mechanism is responsible for both high- T_c superconductivity and "cold-fusion" manifestations is a recent report of low-level neutron production from deuterated high- T_c ceramic superconductor, $\text{YB}_{a_2}\text{Cu}_3\text{O}_7$, below the superconducting transition temperature.^[14]

CONCLUSION

Latent-Heat-of-Water Storage as Practical "New Hydrogen Energy"

Given the latent heat of vaporization content of a gallon of water, approximately 8MJ or 7,600BTU, its electrochemical storage and release by the process described above could be a viable method of hydrogen energy conversion. Ten gallons of water contain approximately 80 MJ or 76,000BTU of latent heat which, if stored and released electrochemically over one hour, approaches the heating capacity of a modest commercial household furnace. To convert this amount of latent heat from 10 gallons of water, would require an electrochemical cell power output of 22KW. Since one cm^3 of Pd (or the equivalent surface area of Ni) is capable, under ideal conditions, of yielding upwards of 1.7KW of stored latent heat,

this would require approximately 13cm³ or 156g Pd, or the equivalent amount of much cheaper Ni. A power of 22KW corresponds to 30HP, suggesting the possibility of a "water engine" electrochemically generating both heat and hydrogen for a fuel cell, which could be used to power or partially power an automobile.

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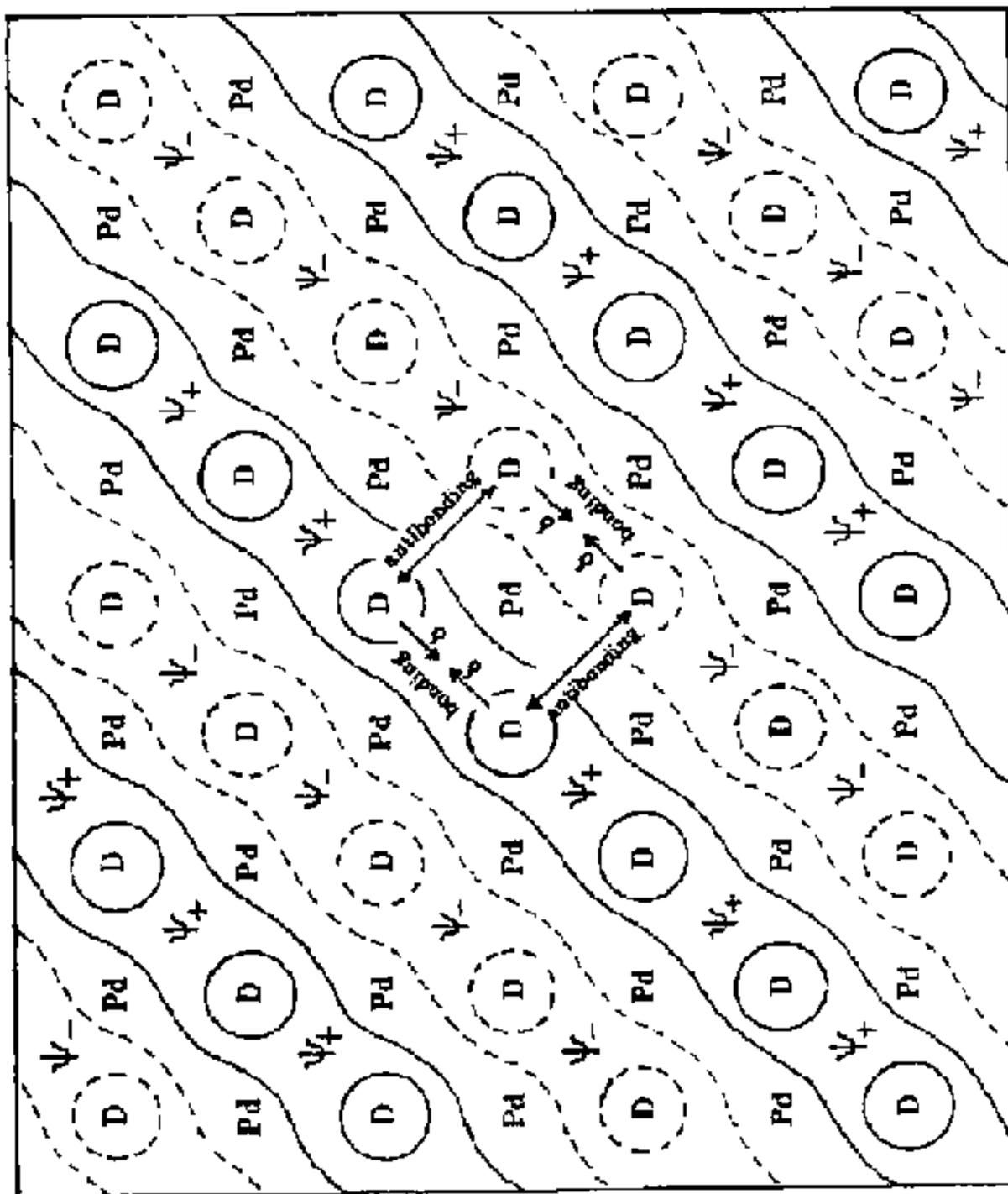


Fig. 1. Schematic representation of D-D bonding "channels" at the Fermi energy (E_F) in γ -PdD. Solid and dashed contours represent positive and negative amplitudes of the wavefunction. The amplitude, δ , of Jahn-Teller-induced D-D vibrations, calculated from Eq. (1), is indicated.

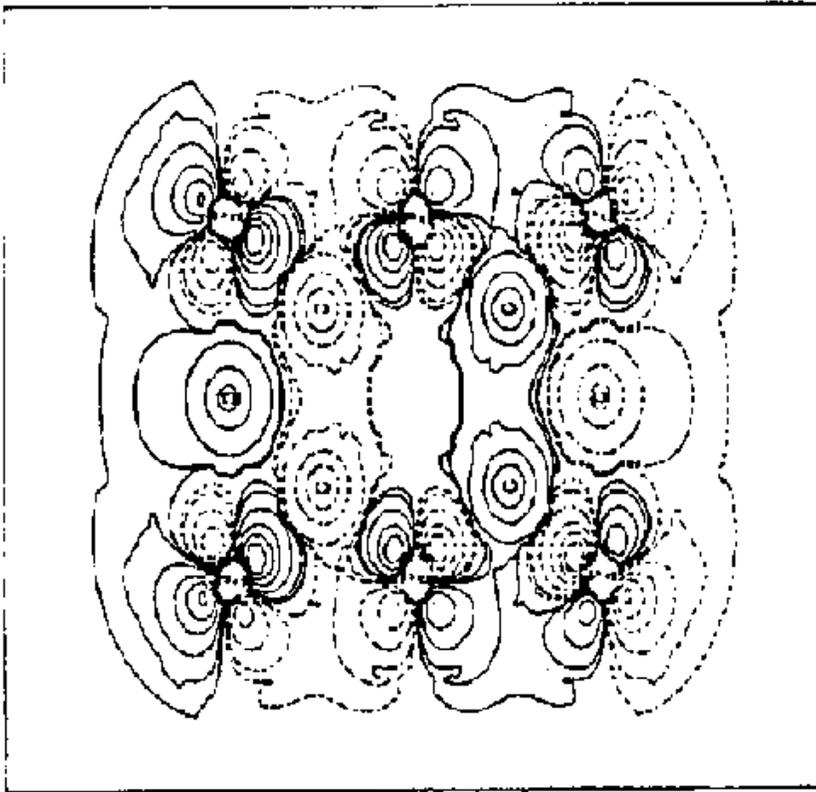


Fig. 2. Density-functional molecular-orbital wavefunction at E_F for γ -PdD plotted in a (110) plane.

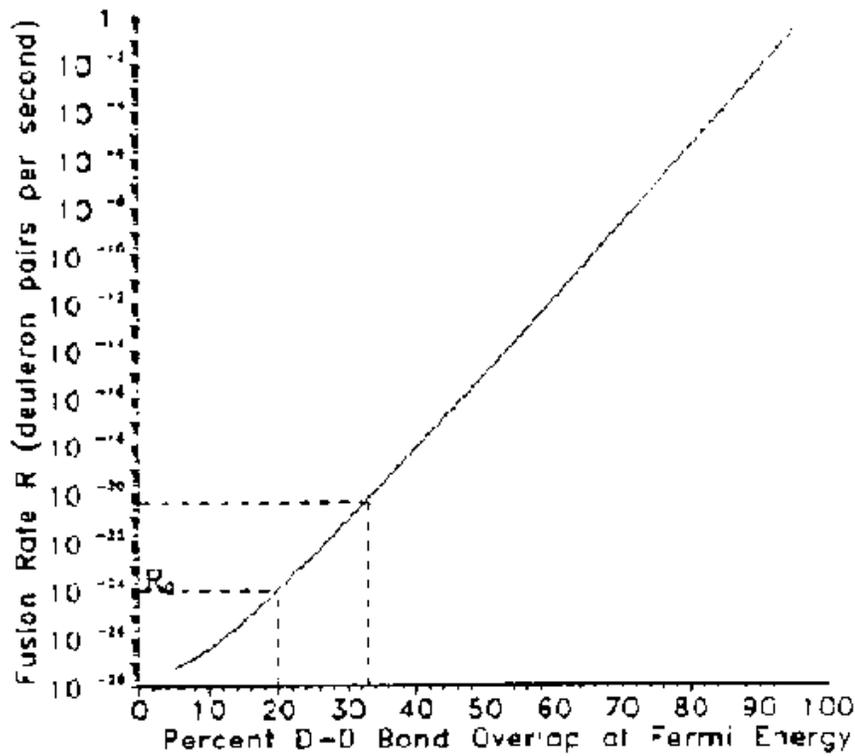


Fig. 3. D-D nuclear fusion rate in γ -PdD induced by the Jahn-Teller effect according to Eq. (2), plotted against D-D bond overlap between tetrahedral sites. The dashed lines bracket the practical limits of fusion.

D-D POTENTIAL SURFACE IN PALLADIUM

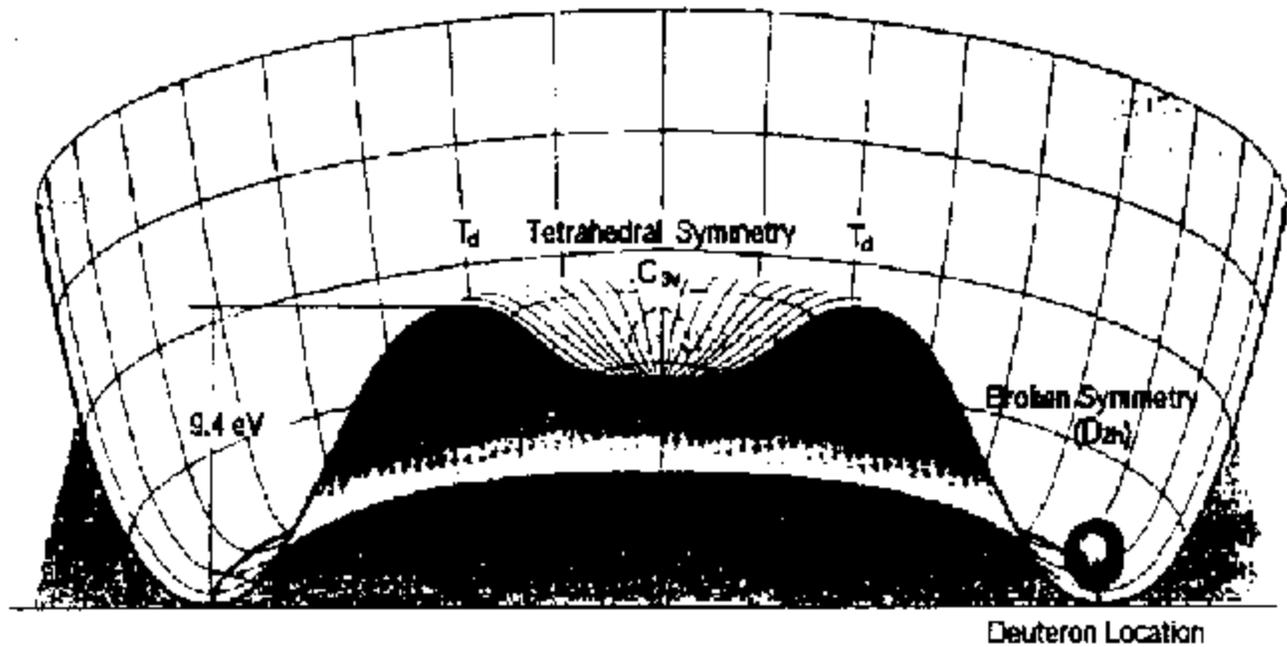


Fig. 4. Schematic "Mexican hat" representation of the D-D potential surface in γ -PdD.

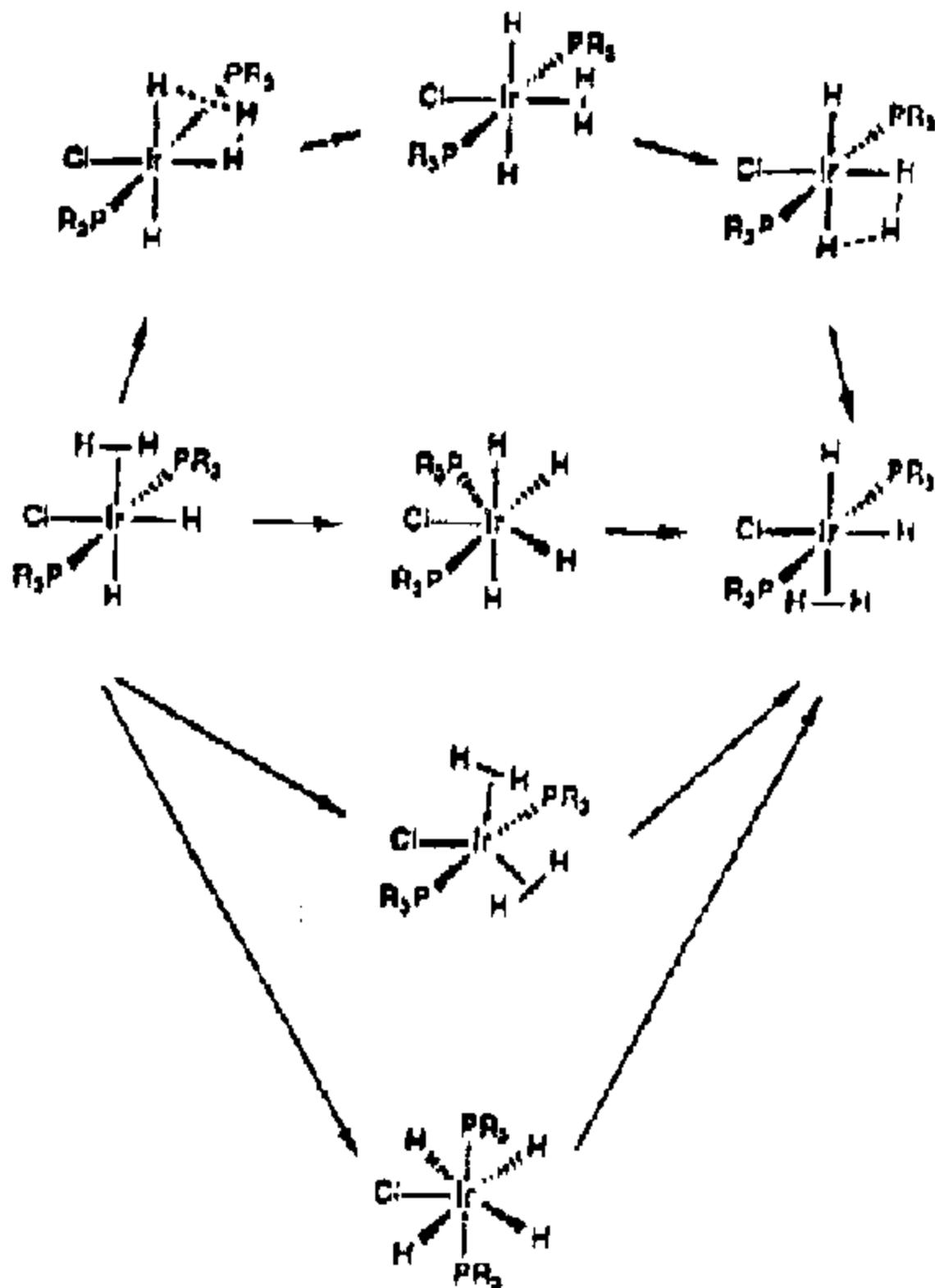


Fig. 5. A molecular analogue of the $4D \rightleftharpoons 2D_2$ process in γ -PdD: the molecular complex $\text{Ir}(\text{PR}_3)_2\text{ClH}_4$, in which the 4H ligands undergo a rapid dynamical dimerization to the dihydrogen dihydride $\text{Ir}(\text{PR}_3)_2\text{ClH}_2\text{H}_2$ (see Ref. 11).

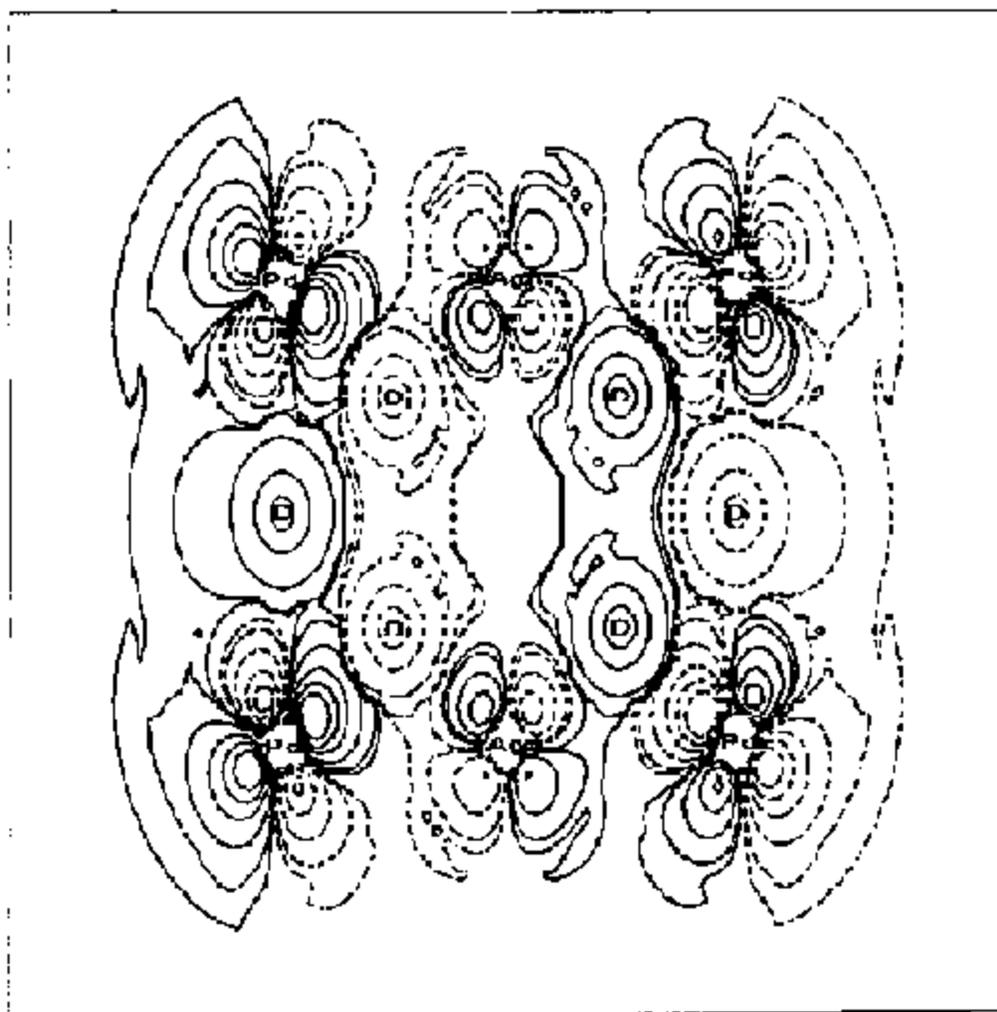


Fig. 6. Density-functional cluster molecular-orbital wavefunction at E_F for γ -Pd_{0.75}Ag_{0.25}D plotted in a (110) plane