

## Models of electronic structure of hydrogen in metals: Pd-H

P. Jena\* and F. Y. Fradin

*Argonne National Laboratory, Argonne, Illinois 60439*

D. E. Ellis

*Northwestern University, Evanston, Illinois 60201*

(Received 16 August 1978; revised manuscript received 12 June 1979)

Local-density theory is used to study the electron charge-density distribution around hydrogen and host palladium metal atoms. Self-consistent calculations using a finite-size molecular-cluster model based on the discrete variational method are reported. Calculations are also done in a simple "pseudojellium" model to study the electron response to hydrogen within the framework of the density-functional formalism. Results of this simple approach agree very well with the molecular-cluster model. Partial densities of states obtained in the cluster model are compared with band-structure results and conclusions regarding the importance of the local environment on the electronic structure are drawn. Calculated core-level shifts and charge transfer from metal ions to hydrogen are compared with the results of x-ray-photoelectron spectroscopy experiments in metal hydrides and are discussed in terms of conventional anionic, covalent, and protonic models. The effect of zero-point vibration on the electron charge and spin-density distribution is studied by repeating the above calculations for several displaced configurations of hydrogen inside the cluster. The results are used to interpret the isotope effect on the electron distribution around proton and deuteron.

### I. INTRODUCTION

The study of the electronic structure of hydrogen in metals is a topic of great current interest. A proton with no core electronic structure is the simplest kind of an impurity that can be implanted into a solid. However, the absence of core electrons results in an effective electron-proton potential that is singular at the proton site. Consequently, the screening of such a strong perturbing impurity cannot be handled well by conventional pseudopotential perturbation theories<sup>1</sup> or statistical methods.<sup>2</sup> Nonlinear theories<sup>3-5</sup> must be used to study the electron response to hydrogen. A knowledge of this nonlinear screening of the proton is useful in understanding the electronic properties of hydrogen in metals. The motivation behind such a microscopic understanding of metal-hydrogen systems is not only academic, but is also due to its practical importance in problems such as embrittlement<sup>6</sup> due to dissolved hydrogen and use of hydrogen in energy-related technology.<sup>7</sup>

In this paper we have studied various electronic properties associated with dissolved hydrogen in transition-metal systems. Although specific calculations are performed for the palladium-hydrogen system, our discussions and conclusions are general and should apply to any metal-hydrogen system. Three common theoretical approaches have been taken: (i) The jellium model—in this model<sup>4,5</sup> (meaningful only for nearly-free-electron systems) the periodic struc-

ture of the host is neglected and the positive charges on the host ions are smeared out uniformly to form a homogeneous background of density  $n_0$ . The screening of a proton is then treated in standard linear<sup>1</sup> or nonlinear screening theories.<sup>3-5</sup> (ii) The band-structure model<sup>8,9</sup>—most applications based on the augmented-plane-wave (APW) method have been used to interpret electronic properties of stoichiometric metal hydrides. Calculations<sup>10</sup> based on the coherent-potential approximation<sup>11</sup> are generally used to study metals containing small amounts of randomly distributed hydrogen. These calculations emphasize the importance of lattice structure. (iii) The molecular-cluster model<sup>12</sup>—this model is somewhat intermediate between the above two models. It is generally assumed that the electronic properties of the impurity are dictated mainly by its local environment. Thus, one treats the impurity and near neighbors as forming a molecular cluster. The eigenstates and electron charge densities are then calculated self-consistently using the local-density approximation. In a metallic environment, the potentials associated with both host and impurity ions are short range due to efficient screening of the ionic charge. Consequently, a molecular-cluster model may provide meaningful results for the electronic structure of impurities in non-free-electron-like systems. Although the above models have been extensively used in the past, it has not been clear which features are model dependent, and which are intrinsic to the impurity

system. A consistent comparison of the results obtained in a *given* system from the different models will, therefore, be useful. In addition, we have extended the scope of both jellium and cluster models to obtain more detailed information about the hydrogen-metal interaction.

Using the above theoretical models, we shall analyze a variety of problems relating to the electronic structure of hydrogen in metals. Historically, there are three simple models<sup>13</sup> that are used to describe the behavior of hydrogen in condensed matter. The *anionic model* is based upon the assumption that an electron from the metal ion is transferred to the hydrogen. In the *covalent hydrogen model*, it is assumed that the hydrogen is covalently bonded to metal ions. In the *protonic model*, the electron is assumed to leave the proton and to participate in filling the occupied metallic band. It is not clear whether any of these descriptions is appropriate for the problem of dilute quantities of hydrogen in metals<sup>14</sup> where screening would certainly play a dominant role. We shall study the possible electron transfer from the metal ion to hydrogen and the accompanying shift in the binding energy of the core levels. Comparison can be made with x-ray-photoelectron spectroscopy<sup>15,16</sup> measurements of the core-level shifts of the metal ion in the hydride phase compared to that in the pure metallic state.

Through nuclear-magnetic-resonance experiments,<sup>17</sup> the proton spin-lattice relaxation time is used to provide information on the contact spin density at the hydrogen site. A comparison of this with the deuteron spin-relaxation rate in metal deuterides yields information on the isotope effect.<sup>18</sup> The proton and deuteron are both light impurities, and the effect of their zero-point vibration on the electronic structure will be discussed.

The outline of the paper dealing with the discussion of the above properties is as follows: In Sec. II we discuss the self-consistent density-functional formalism for an inhomogeneous electron gas. We prescribe a homogeneous-density scheme for treating the screening of hydrogen in non-free-electron-like metals. This model can be viewed as a pseudojellium model. In Sec. III, the essentials of the molecular cluster approach are outlined. The results of electron charge distribution around a hydrogen atom along different crystallographic directions obtained in the above two models are compared in Sec. IV. This section also contains a comparison of the partial density of states obtained in our molecular-cluster model with that of the APW band-structure approach. The problem of charge transfer from metal ion to hydrogen is discussed in Sec. V in the light of recent experiments using x-ray-photoelectron spectroscopy. In Sec. VI we discuss the effect of zero-point vibration on the electron charge and spin distribution around a light impurity. Our results are summarized in Sec. VII.

## II. HOMOGENEOUS-DENSITY APPROXIMATION TO MOLECULAR CLUSTERS: A PSEUDOJELLIUM MODEL

In this section we prescribe a scheme to study the screening of a proton in a non-free-electron-like metal. In the conventional jellium approach, the electron density of the homogeneous background is given by a density parameter  $r_s$ , where

$$\frac{4}{3}\pi(r_s a_0)^3 = 1/n_0 \quad (1)$$

The conduction-electron density,  $n_0$ , is determined by accounting for the number of "free" electrons,  $Z$  (usually the valence) per atomic volume,  $\Omega_0$ , i.e.,  $n_0 = Z/\Omega_0$ . The electron distribution around the proton is then studied by embedding the point charge in this homogeneous medium. In extending this scheme to non-free-electron-like systems, the first difficulty is to estimate the quantity,  $Z$ . In keeping with the spirit of the jellium model, one should integrate the  $sp$  component of the electron density of states up to the Fermi energy  $E_F$  to estimate  $Z$ . This obviously requires a prior knowledge of the partial density of states obtained in the band-structure calculation. In addition, one assumes that the interaction between the impurity and the host  $d$  electrons is negligible.

In the following we suggest an alternate scheme. To determine the ambient electron charge density  $\bar{n}_0(\bar{r})$  of the perfect host at any point in space to a first approximation, we use the noninteracting atom model. In this model,

$$\bar{n}_0(\bar{r}) = \sum_{\nu} n_0(\bar{r} - \bar{R}_{\nu}) \quad (2)$$

where  $n_0(\bar{r} - \bar{R}_{\nu})$  is the free-atom charge density centered on the  $R_{\nu}$ th lattice site and can be computed from a knowledge of the one-electron orbitals,<sup>19</sup>  $\psi_{nlm}(\bar{r})$ , namely,

$$\begin{aligned} n_0(\bar{r}) &= \sum_{nlm} |\psi_{nlm}(\bar{r})|^2 \\ &= 2 \sum_{nl} \frac{2l+1}{4\pi} R_{nl}^2(r) \quad (3) \end{aligned}$$

where  $2(2l+1)$  is the spin and orbital degeneracy factor and  $R_{nl}(r)$  is the radial wave function of the quantum state  $nl$ . Thus, the density parameter  $r_s$  is itself a function of  $r$ , i.e.,  $\frac{4}{3}\pi r_s^3(\bar{r}) a_0^3 = 1/\bar{n}_0(\bar{r})$ . In palladium (fcc) crystal, for example, the proton is known to occupy the octahedral site. The ambient density at this point can be evaluated from Eq. (2). In practice, however, it is sufficient to consider only the nearest-neighbor host ions since the second and further out neighbors make a negligible contribution to the ambient electron density.

Having determined the ambient electron density at a point  $\bar{r}$ , in space, the response of the electrons to a

proton at that point is calculated by assuming that the electrons respond to the proton as if the proton is situated in a *homogeneous* electron gas of density  $\bar{n}_0(\bar{r})$ . This model will be referred to as the "pseudojellium" model and is obviously an approximation to a more complicated molecular-cluster model (discussed in Sec. III) where hydrogen and the surrounding metal ions are allowed to interact among each other in establishing the ground-state distribution of the electron density. The justification for the use of this pseudojellium model can only be made after comparing the results (see Sec. IV) with that obtained in the more sophisticated molecular-cluster model.

We have used the density-functional formalism<sup>20,21</sup> of Hohenberg, Kohn, and Sham (HKS) to treat the screening of the proton in the pseudojellium model. Much has been written about the HKS theory and we refer the reader to the recent papers by Jena *et al.*<sup>5,22</sup> for further details. The numerical work for the density-functional formalism has been carried out in a manner described earlier.<sup>5,22</sup> The charge density  $n(\bar{r})$  and spin-density  $n^\sigma(\bar{r})$  distribution around hydrogen have been calculated self-consistently to a precision of better than 2% in  $n^\sigma(r)$  in the vicinity of the proton.

### III. SELF-CONSISTENT MOLECULAR-CLUSTER MODEL

We also use the local-density formalism described earlier in carrying out molecular-orbital (MO) calculations on finite clusters representative of the solid. The MO eigenstates are expanded as a linear combination of atomic orbitals,

$$\psi_n(\bar{r}) = \sum_j a_j(\bar{r} - \bar{R}_j) C_{jn} \quad (4)$$

The variational coefficients  $\{C_{jn}\}$  are obtained by solving the secular equation of the discrete variational method.<sup>12</sup> This method has been described in detail elsewhere.<sup>12,23,24</sup> Here, we only note that the single-particle equation,

$$(h_\sigma - \epsilon_{n\sigma})\psi_{n\sigma}(\bar{r}) = 0 \quad (5)$$

is approximately solved by minimizing certain error moments on a sampling grid in  $\bar{r}$ . The effective Hamiltonian for states of spin  $\sigma$  is given by

$$h_\sigma = t + V_{\text{Coul}} + V_{\text{exch},\sigma} \quad (6)$$

where the first two terms are the kinetic energy and Coulomb potential. The exchange potential is taken in the usual form,

$$V_{\text{exch},\sigma} = -6\alpha[3n_\sigma(\bar{r})/4\pi]^{1/3} \quad (7)$$

The value  $\alpha = 0.7$ , close to that of Kohn and Sham,

was used in all calculations. There exist more elaborate local-density exchange and correlation potentials which are found to lead to small differences in self-consistent energy levels and charge densities for transition metals.<sup>25</sup> These differences are too small to be of any consequence for the present work.

Calculations were made for the octahedral Pd<sub>6</sub> and Pd<sub>6</sub>H clusters with bond length taken for the bulk Pd metal. The proton was placed either at the (0,0,0) octahedral site, or displaced along the [100] direction. A spin-restricted (assuming  $n_\sigma = \frac{1}{2}n$ ) model was used, with the iteration procedure starting from superimposed atomic charge densities. Interaction of the cluster with the crystalline environment was ignored, since we plan to concentrate on properties associated with the center of the cluster. However, for any reasonable treatment of bulk metal properties, it is necessary to embed the cluster in an effective medium.<sup>26</sup> In order to compare these results with band-structure calculations and experiments on stoichiometric PdH, it is necessary to study the sensitivity of our calculated electron densities around hydrogen to its chemical environment. We have, therefore, repeated our pseudojellium calculations by considering the lattice parameters and geometrical arrangements of Pd and H in PdH. The decrease in the ambient charge density due to the surrounding Pd atoms in PdH as a result of lattice expansion is found to be somewhat compensated by the additional contribution of the hydrogen atoms to the ambient charge density. As a result, the calculated self-consistent electron density at the hydrogen site in PdH does not differ significantly from that of a single octahedrally coordinated hydrogen atom in pure Pd. This calculation was not repeated for the self-consistent molecular-cluster model. However, we do not expect the results to be qualitatively different. Thus, the comparison of the electronic properties associated with hydrogen, in Secs. IV–VI, in the pseudojellium and molecular-cluster models with band-structure calculations and experiments on PdH is meaningful.

### IV. COMPARISON BETWEEN PSEUDOJELLIUM, MOLECULAR-CLUSTER, AND BAND-STRUCTURE MODELS

This section is divided into two parts. First, we discuss the electron charge density around a proton octahedrally coordinated to six neighboring Pd atoms obtained self-consistently in both the pseudojellium and molecular-cluster model. Second, the partial density of states obtained in the molecular-cluster approach will be compared with APW band-structure calculations.<sup>9</sup>

In Fig. 1 we present a comparison of the ambient charge density obtained by a superposition of the

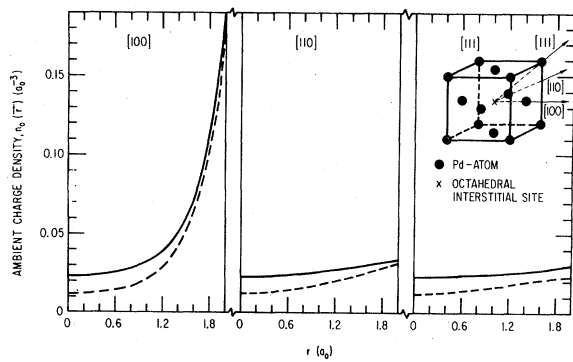


FIG. 1. Electron charge-density distribution inside the unit cell of Pd. The solid line represents a self-consistent molecular-cluster calculation based on a six-Pd-atom cluster; the dashed line is obtained by a linear combination of free-atom charge densities centered at individual nuclear sites of the above cluster. The octahedral site (equilibrium configuration of hydrogen given by  $\times$ ) defines the origin of the real-space coordinate system.

free-atom charge densities (dashed curve) with that calculated in the molecular-cluster model consisting of six interacting Pd atoms located at the face centers of the cube (solid curve). At the octahedral site (taken as the origin) the charge density due to the interacting metal atoms is about a factor of 2 larger than that due to the simple superposition model. The anisotropy remains small, as expected, for distances up to  $1a_0$  (Bohr radius) from the origin. However, for farther distances, the charge density along the [100] direction increases much more rapidly than along the [110] and [111] directions since the nearest-neighbor Pd atom lies along the [100] direction. This anisotropy in the ambient charge distribution is also apparent from the simple noninteracting atom model.

The electron distribution around a proton embedded at the octahedral interstitial site in Pd metal is calculated self-consistently in the pseudojellium model and is compared with the molecular-cluster ( $\text{Pd}_6\text{H}$ ) result in Fig. 2. The electron densities at the proton site in these two calculations differ from each other by about 17% while the discrepancy gets narrower as one goes farther away from the proton. The charge distribution remains isotropic within a sphere of one Bohr radius around the proton. This result along with the agreement between pseudojellium and molecular-cluster models may, at first, be surprising. An analysis of the different angular momentum components of the charge density based on the jellium model reveals that the electrons around the proton have predominantly  $s$  symmetry. This result is consistent with the angular momentum resolved partial density of states for the  $\text{Pd}_6\text{H}$  cluster inside the hy-

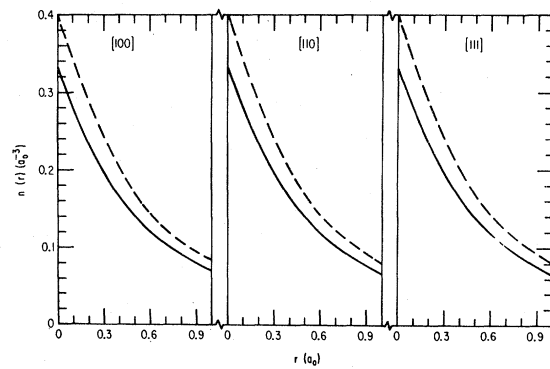


FIG. 2. Comparison between the electron charge densities along the [100], [110], and [111] directions around an octahedrally coordinated hydrogen atom calculated self-consistently in the molecular-cluster (solid curve) and pseudojellium (dashed curve) models.

drogen sphere (see below) as well as with the predominant  $s$ -wave scattering from the hydrogen determined from de Haas-van Alphen experiments<sup>27</sup> in copper containing dilute amounts of hydrogen. If one were to use the ambient density at the octahedral position in Pd from the molecular-cluster calculations for the  $\text{Pd}_6$  complex instead of that obtained from the noninteracting atom model, the pseudojellium model for Pd-H would yield an electron density at the proton site that is 35% higher than the  $\text{Pd}_6\text{H}$  cluster calculation. However, with this approach the pseudojellium model loses its attractiveness, since the required  $\text{Pd}_6$  cluster calculation needed to determine the ambient density is as difficult as the full  $\text{Pd}_6\text{H}$  calculation. It is interesting that the charge density at the proton site in the pseudojellium model is higher than that obtained in the molecular-cluster calculation. This result is consistent with one's physical intuition that in the molecular-cluster model, a fraction of the electrons around hydrogen will be pulled away to screen the Pd atoms and to form the Pd-H bond as well. In addition, the pseudojellium model treats the ambient interstitial electrons as free-electron-like. Since the interstitial density includes a  $d$ -state contribution and the  $d$  electrons are less polarizable than  $s$  electrons of the same density, the pseudojellium model would tend to overestimate the proton screening.

To compare the energy eigenvalues of electrons between molecular-cluster and band-structure models, we use the concept of partial density of states (PDOS). We decompose the charge density into contributions from different sites and obtain information about the metal-hydrogen bond. In addition, it is possible to make a comparison with the PDOS found in APW band-structure calculations<sup>9</sup> on stoichiometric PdH. The cluster PDOS is found as a

sum of Lorentzian lines of width  $\gamma$  centered at the molecular-orbital energies,

$$D_n(E) = \sum_j f_{nj} \frac{\pi/\gamma}{(E - E_j)^2 + \gamma^2} \quad (8)$$

Here  $\gamma$  was chosen as 0.4 eV (consistent with the discrete level structure of the cluster and uncertainty of  $\sim 0.1$  eV in cluster levels due to basis-set limitations), and  $f_{nj}$  were taken to be atomic populations obtained from a Mulliken population analysis<sup>28</sup> of the eigenvectors. The cluster PDOS for Pd 4*d* and hydrogen 1*s* states are shown in Fig. 3. The Pd-H bonding band centered at  $\sim 8$  eV below the Fermi energy has a strong resemblance to that found for the ordered compound by the APW method.<sup>9</sup> This suggests that these very different models are converging

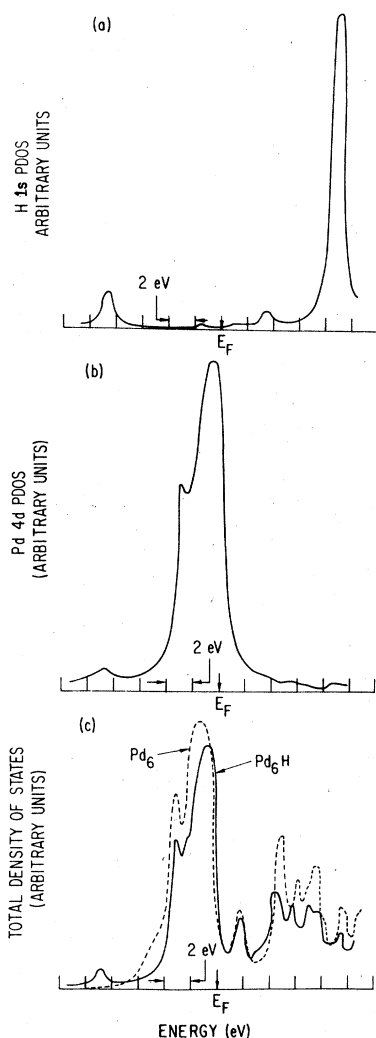


FIG. 3. Partial density of states in arbitrary units for (a) hydrogen 1*s*, (b) Pd 4*d* states, and (c) total density of states for Pd<sub>6</sub>H (solid line), and Pd<sub>6</sub> (dotted line) clusters.

upon a common description. The total density of states for the cluster, containing sizable metal *sp* contributions, is also shown in Fig. 3. With the main features aligned to remove level shifts due to small cluster size, we see that the density of states for Pd<sub>6</sub> and Pd<sub>6</sub>H clusters differs little, except for the bonding Pd-H peak noted in the PDOS curves. We now turn to a discussion of the electron-spin density at the proton site in PdH as obtained from band-structure and pseudojellium models.

Using the method in Sec. II, we have calculated the spin-density enhancement,  $[n \uparrow(0) - n \downarrow(0)] / (n \uparrow - n \downarrow)$  at the hydrogen site in Pd to be 10.7. The corresponding band-theory result<sup>9</sup> for PdH is 6.8. A critical comparison between the pseudojellium and the band-theory result for the spin density is hampered since the APW band-structure<sup>9</sup> calculation was not carried out self-consistently. It is, however, encouraging that our result is in semiquantitative agreement with band calculation. Neglect of a periodic arrangement of Pd atoms in the pseudojellium model gives rise to a spin density that is larger in magnitude than the band-theory result. This systematic trend, as described in Sec. IV, also exists in the charge density at the proton site.

The nuclear-spin-lattice relaxation rate at the hydrogen site calculated in the pseudojellium model (with the *s* density of states at the Fermi energy taken from band-theory result) is about 57% higher than experiment.<sup>17,18</sup> It is worth mentioning that the Knight shift (which also measures the spin density) at the positive muon (a light isotope of hydrogen) sites in paramagnetic metals calculated<sup>5</sup> in the jellium model are consistently higher than the corresponding experimental values.<sup>29</sup> Thus, the jellium model is found to consistently overestimate the electron charge and spin density at the hydrogen site. The effect of introducing the periodic array of metal ions would be to reduce the magnitude of these electron densities—a trend in the right direction for explaining the experimental data.

## V. CHARGE TRANSFER AND CORE-LEVEL SHIFTS DUE TO HYDROGENATION

This section deals with a discussion of models of the chemical bond between hydrogen and metal ions and the effects associated with possible charge transfer from the metal ions to hydrogen. In solving the set of self-consistent HKS equations<sup>20</sup> in Sec. II, we have found that the effective potential is strong enough to form weakly bound states with two electrons as have been found earlier by several workers<sup>4,5,22</sup> throughout the metallic density range. Even though single-particle eigenvalues have no fundamental meaning in HKS theory, the whole of band theory based on HKS formalism rests on their in-

terpretation. The spin  $\uparrow$  and spin  $\downarrow$  bound-state wave functions extend over several lattice spacings, supporting the picture that the electronic structure of hydrogen in metals is that of an extended  $H^-$  ion<sup>5</sup> with an equally extended hole in the continuum. Since the calculated lifetime broadening<sup>30</sup> of these states due to electron-electron interaction is large compared

to their binding energies, the physical significance of these bound states is not well established. As a matter of fact, experiments using positive muons<sup>31</sup> designed to look for these bound states have been unsuccessful.

In order to provide a more physical understanding of the electronic configuration of hydrogen in a metallic environment, we compute the difference in the electron density around the octahedral site between the  $Pd_6H$  and  $Pd_6$  cluster, i.e.,

$$\Delta n(\vec{r}) = n_{Pd_6H}(\vec{r}) - n_{Pd_6}(\vec{r}) . \quad (9)$$

This difference, indicative of charge readjustment due to hydrogenation is plotted in Fig. 4(a) along the [100] direction for the molecular-cluster calculation. The negative region of electron density for distances beyond  $\sim 2$  Bohr radii suggests that the charge from the vicinity of the metal ion has been transferred to the hydrogen sphere. Thus, a comparison of the number of electrons,  $Z(R)$ , contained in a sphere of radius  $R$  around the proton in a metal,

$$Z(R) = \int_0^R d^3r \Delta n(\vec{r}) , \quad (10)$$

with that of free-hydrogen atom would indicate the extent of excess screening of hydrogen. This result as shown in Fig. 4(b) for the similar case of H in Zr ( $r_s = 2.7$ ) is also apparent from our pseudojellium model. Since  $Z(\infty)$  has to be equal to unity in all calculations to ensure electrical charge neutrality, the observed charge transfer could be described as the hydrogen being slightly anionic and the metal ion being slightly cationic.

A direct consequence of the reduction of electrons around the metal ion is to alter the core-level energies. In Table I we compare the energies of the  $4p$ ,  $4s$ , and  $3d$  core levels of the palladium atom in the

TABLE I. Comparison of Pd core-level energies (eV) relative to Fermi energy<sup>a</sup> of atom and cluster in nonrelativistic self-consistent local-density model.

Level	Atom	$Pd_6$	$Pd_6H$
$4p$	46.3	46.7	47.0
$4s$	75.5	75.9	76.2
$3d$	328.3	329.2	329.5

<sup>a</sup>Here we define the Fermi energy to be the eigenvalue of the last occupied level. By relating the core energies of the atom and various clusters to their respective Fermi energies, we compensate for shifts in binding energies which are model dependent, i.e., depend upon cluster size and boundary conditions. This procedure makes it possible to use ground-state eigenvalues to estimate binding energies, as an alternative to excited state or transition state (see Ref. 34) calculations needed to determine absolute binding energies.

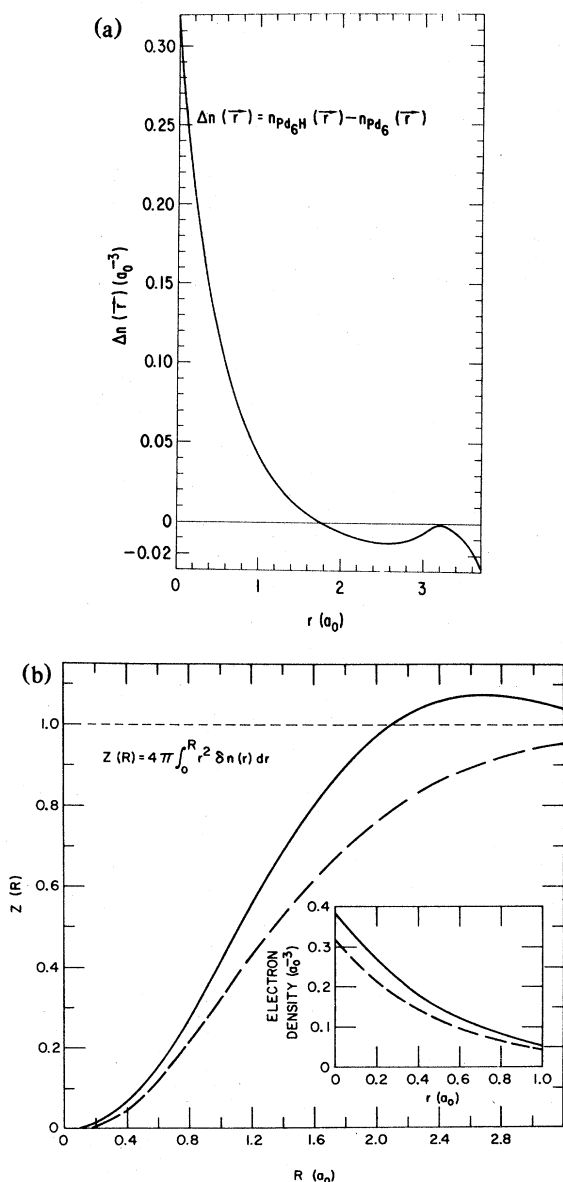


FIG. 4. (a) Difference in the electron charge density in  $Pd_6H$  and  $Pd_6$  clusters. The negative region indicates the zone from which metal charge has been transferred due to hydrogenation. (b) Number of electrons contained in a sphere of radius  $R$  around a proton embedded in a jellium of  $r_s = 2.7$  (corresponding to hydrogen tetrahedrally bonded to Zr atoms) (solid curve) vs that around a proton in free-hydrogen atom (dashed curve).

free-atom, and Pd<sub>6</sub> Pd<sub>6</sub>H cluster configurations. In the six-Pd-atom cluster, some charge from each atom is donated to the conduction sea resulting in an increase of about 0.4 eV in the ion core levels. The addition of hydrogen accentuates this trend. The Pd-H bonding charge is being drawn from the vicinity of the metal ion core [see Fig. 4(a)], leaving core levels still more tightly bound.

This effect has been seen in a recent experiment by Veal *et al.*<sup>16</sup> involving x-ray-photoelectron spectroscopy. These authors have compared the core-level shifts of Zr 4*p* and 3*d* levels in ZrH<sub>1.65</sub> with that in pure Zr and find that the levels shift to higher binding energies by 0.7 and 1 eV, respectively. This result is consistent with our cluster calculation in the Pd-H system. A quantitative comparison of these core-level shifts at this stage is unwarranted since we expect these shifts to depend on the local environment. In the hydride phase, for example, the concentration of hydrogen is high. Thus, we expect the magnitude of shifts in Table I due to hydrogenation to be significantly larger than the present estimate. As pointed out earlier, the molecular cluster has to be embedded in a potential background simulating the crystalline environment. We are presently carrying out these calculations for several transition-metal hydrides.

## VI. ISOTOPE EFFECT ON THE ELECTRON DISTRIBUTION AROUND <sup>1</sup>H AND <sup>2</sup>D

Studies of neutron inelastic scattering<sup>32,33</sup> on metals containing hydrogen reveal localized modes for hydrogen which in palladium occurs at 56 meV. Assuming that the proton moves in a harmonic potential well, this localized mode corresponds to a mean-square hydrogen vibration amplitude of 0.07 Å<sup>2</sup>. In this section we discuss briefly the effect of this zero-point vibration on the electron distribution around the point charge.

Jena *et al.*<sup>18</sup> have recently analyzed the isotope effect using a semiempirical model based on the band-structure calculation and a first principles calculation based on the pseudojellium model. They have shown that these two distinctly different models yield physically similar results on the electron-spin density at <sup>1</sup>H and <sup>2</sup>D sites in PdH. The results successfully explained the higher nuclear spin-lattice relaxation rate<sup>17</sup> of <sup>2</sup>D compared to <sup>1</sup>H as due to larger zero-point vibrational amplitude of hydrogen. The reader is referred to the paper of Jena *et al.*<sup>18</sup> for details. In this section we make a comparison of the electron charge distribution around a displaced proton obtained in both the pseudojellium and molecular-cluster models. This comparison should provide some insight into the quantitative significance of the results of the pseudojellium calculation.

In order to gauge the reliability of the pseudojellium model in interpreting effects associated with the zero-point vibration, we have carried out the molecular-cluster calculation (see Sec. III) for four different configurations of the hydrogen atom inside the Pd octahedron, i.e., the equilibrium site and configurations of hydrogen displaced by 0.3*a*<sub>0</sub>, 0.8*a*<sub>0</sub>, and 1.2*a*<sub>0</sub> along the [100] axis. The results are plotted in Fig. 5.

The fact that the electrons follow the proton faithfully can be seen from the figure. Two other interesting points are worth noting. First, the electron charge distribution around the proton is very close to being isotropic even for a proton displaced by as much as 0.8*a*<sub>0</sub> from the equilibrium configuration. Second, the electron density at the proton site as a function of displacement (see inset of Fig. 5) increases rapidly as the proton approaches the nearest-neighbor Pd atom. While the ambient density at a point 1.2*a*<sub>0</sub> from the equilibrium configuration along the [100] direction increases by a factor of 2 (see Fig. 1) the self-consistent proton-site density increases by more than a factor of 3 (see Fig. 5). This enhancement can be attributed to the formation of a stronger Pd-H bond as the nearest-neighbor Pd-H distance is reduced to 2.4*a*<sub>0</sub>. A similar displacement in other directions produces a smaller enhancement. This anisotropy of the proton environment is primarily responsible for the deviation between the pseudojellium and the cluster results for large proton displacements.

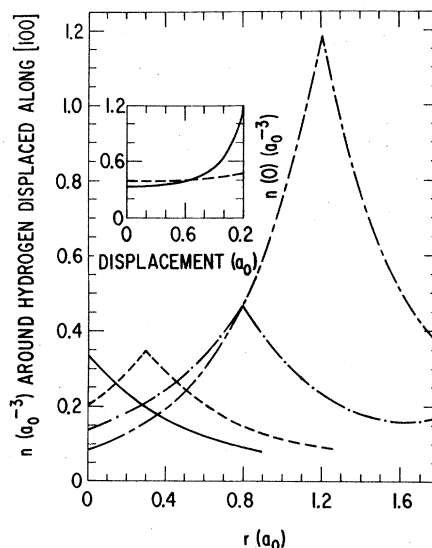


FIG. 5. Self-consistent molecular-cluster result for electron charge-density distribution along the [100] direction around a hydrogen atom located at (0,0,0) (—curve), (0.3,0,0) (---curve), (0.8,0,0) (-·-·-curve), and (1.2,0,0) (---curve). The inset shows a comparison between the electron charge density at the proton site in a molecular-cluster (solid curve) and pseudojellium (dashed curve) models.

To compare the above results with the predictions of the pseudojellium model, we have followed the same procedure as outlined for the spin density. The results are compared with the molecular-cluster model in the inset of Fig. 5. Note that both the calculations are in close agreement with each other for displacements up to  $0.5a_0$  from the equilibrium configuration. However, for larger displacements, the pseudojellium model fails to account for the sharp rise in the electron charge density at the proton site. The configuration-averaged charge density following the prescription of Jena *et al.*<sup>18</sup> in the molecular-cluster model is  $0.35/a_0^3$ , whereas it is  $0.405/a_0^3$  in the pseudojellium model. The nature of this agreement between two models is similar to that at the equilibrium configuration discussed earlier. This close agreement between the configuration-averaged charge densities (in spite of the large discrepancy for larger displacements) is not surprising since the probability of the proton being at a displaced position becomes considerably smaller as the displacement increases. It is encouraging that the pseudojellium model gives not only qualitatively the same result for the configuration-averaged charge density as the more sophisticated molecular-cluster model, but it is also in semi-quantitative agreement with the latter. It is to be noted that cluster calculations will be quantitatively influenced by both cluster size and boundary condition. A 10% deviation is a reasonable estimate of these effects. Calculations of electron-spin density at the proton site in the molecular-cluster model, including effects due to zero-point vibration, are not available at the present time to compare with the pseudojellium model. However, we do not expect any major differences.

### VIII. CONCLUSION

In this paper we have attempted to give a comprehensive discussion of the electronic structure of hydrogen in metals. Although specific calculations for the Pd-hydrogen system were performed, the theoretical models and subsequent discussions are applicable to a general metal-hydrogen system. Our results are summarized in the following:

(i) A homogeneous density response model within the framework of density-functional formalism<sup>20,21</sup> was used to calculate the nonlinear electron charge and spin distribution around hydrogen in palladium. The results were compared with our self-consistent molecular-cluster model. The charge density in the vicinity of the proton in these two models is found to agree to within 12%. We, therefore, suggest that for semiquantitative analysis, our pseudojellium

model would serve as an efficient calculational method. This model is particularly attractive when one realizes that the numerical effort is considerably less than that involved in a self-consistent molecular-cluster calculation<sup>12</sup> let alone that in a self-consistent supercell band calculation.<sup>14</sup> The electron-spin density at the proton site in the Pd-H system was found to be in fair agreement with the non-self-consistent band calculation<sup>9</sup> for PdH.

(ii) A comparison between our molecular-cluster calculation and the band structure indicates agreement in the nature of the palladium-hydrogen bond and in the qualitative shape of the partial density of states.

(iii) From a comparison of the electron charge distribution around palladium in its pure state with that upon hydrogenation, we find that there is a significant charge transfer from the vicinity of the metal ion to the hydrogen sphere. This consequently results in a shift in the core-level binding energies of the metal ion in the hydride phase towards higher binding as compared to its pure state. This result is consistent with a similar effect observed<sup>16</sup> in  $ZrH_{1.65}$  from x-ray-photoelectron spectroscopy measurements. The resulting excess electron density around hydrogen in a metallic environment compared to that in free space gives rise to a physical picture that hydrogen in metals remains in a slightly "anionic" state.

(iv) The electron-spin density at the equilibrium proton site was calculated self-consistently using the generalized density-functional formalism.<sup>21</sup> Combined with the energy-band density of states of *s* electrons at the Fermi energy, this calculation yielded the proton spin-lattice relaxation rate that was 57% higher than the experimental value.<sup>17</sup> The effect of the finite mass of the proton and deuteron on the electron charge and spin distribution of the surrounding electrons was studied in PdH and PdD in two distinctly different models. Both calculations yield a larger electron-spin density at the <sup>2</sup>D site than at the <sup>1</sup>H site—a result in agreement with recent experimental data. The effect of zero-point vibration on the electronic structure was also studied in the self-consistent molecular-cluster model for various displacements of the proton. The time-averaged charge density at the proton site was found to be in good agreement with the pseudojellium model.

### ACKNOWLEDGMENT

This work supported by the U. S. Department of Energy. D. E. Ellis is also supported by the NSF through Grant No. DMR77-22646. We are thankful to Dr. S. K. Sinha, B. W. Veal and D. J. Lam for many stimulating discussions.



- \*Present address: Phys. Dept., Mich. Techno. Univ., Houghton, Mich. 49931.
- <sup>1</sup>W. A. Harrison, *Pseudopotential in Theory of Metals* (Benjamin, New York, 1966).
- <sup>2</sup>L. H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1927); E. Fermi, Z. Phys. **48**, 73 (1928).
- <sup>3</sup>J. Friedel, Philos. Mag. **43**, 153 (1952); A. Sjölander and M. J. Stott, Phys. Rev. B **5**, 2109 (1972); P. Bhattacharya and K. S. Singwi, Phys. Rev. Lett. **29**, 22 (1972); A. K. Gupta, P. Jena, and K. S. Singwi, Phys. Rev. B **18**, 2712 (1978).
- <sup>4</sup>Z. D. Popović, M. J. Stott, J. P. Carbotte, and G. R. Piercy, Phys. Rev. B **13**, 590 (1976); C. O. Almbladh, U. von Barth, Z. D. Popović, and M. J. Stott, Phys. Rev. B **14**, 2250 (1976); E. Zaremba, L. M. Sander, H. B. Shore, and J. H. Rose, J. Phys. F **7**, 1763 (1977).
- <sup>5</sup>P. Jena and K. S. Singwi, Phys. Rev. B **17**, 3518 (1978).
- <sup>6</sup>B. A. Kolachev, *Hydrogen Embrittlement of Nonferrous Metals* (Israel Program for Scientific Translation, Jerusalem, 1968).
- <sup>7</sup>J. J. Reilly, Jr., in *Proceedings of the International Symposium on Hydrides for Energy Storage, Geilo, Norway, 1977*, edited by A. F. Anderson and A. J. Maelland (Pergamon, Oxford, 1978).
- <sup>8</sup>D. A. Papaconstantopoulos and B. M. Klein, Phys. Rev. Lett. **35**, 110 (1975); B. M. Klein, E. N. Economou, and D. A. Papaconstantopoulos, Phys. Rev. Lett. **39**, 574 (1977); D. A. Papaconstantopoulos, B. M. Klein, E. N. Economou, and L. L. Boyer, Phys. Rev. B **17**, 141 (1978).
- <sup>9</sup>M. Gupta and A. J. Freeman, Phys. Rev. B **17**, 3029 (1978).
- <sup>10</sup>C. D. Gelatt, Jr., H. Ehrenreich, and J. A. Weiss, Phys. Rev. B **17**, 1940 (1978); J. S. Faulkner, Phys. Rev. B **13**, 2391 (1976).
- <sup>11</sup>H. Ehrenreich and L. M. Schwartz, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1976), Vol. 31, p. 149.
- <sup>12</sup>E. J. Baerends, D. E. Ellis, and P. Ros, Chem. Phys. **2**, 41 (1973).
- <sup>13</sup>See the review by W. M. Mueller, J. P. Blackledge, and G. Libowitz, *Metal Hydrides* (Academic, New York, 1968); G. G. Libowitz, Ber. Bunsenges. Phys. Chem. **76**, 705 (1972).
- <sup>14</sup>A. C. Switendick, Solid State Commun. **8**, 1463 (1970); Int. J. Quant. Chem. **5**, 459 (1971); Ber. Bunsenges. Phys. Chem. **76**, 535 (1972).
- <sup>15</sup>See *Photoemission in Solids I*, edited by M. Cardona and L. Ley (Springer-Verlag, Heidelberg, 1978).
- <sup>16</sup>B. W. Veal, D. J. Lam, and D. G. Westlake Phys. Rev. B **19**, 2856 (1979).
- <sup>17</sup>C. L. Wiley and F. Y. Fradin, Phys. Rev. B **17**, 3462 (1978).
- <sup>18</sup>P. Jena, C. L. Wiley, and F. Y. Fradin, Phys. Rev. Lett. **40**, 578 (1978).
- <sup>19</sup>E. Clementi and C. Roetti, At. Data Nucl. Data **14**, 177 (1974).
- <sup>20</sup>P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
- <sup>21</sup>U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972); A. K. Rajagopal and J. Callaway, Phys. Rev. **137**, 1912 (1973).
- <sup>22</sup>P. Jena, K. S. Singwi, and R. Nieminen, Phys. Rev. B **17**, 301 (1978).
- <sup>23</sup>F. W. Averill and D. E. Ellis, J. Chem. Phys. **59**, 6412 (1973).
- <sup>24</sup>A. Rosén and D. E. Ellis, J. Chem. Phys. **65**, 3629 (1976).
- <sup>25</sup>C. S. Wang and J. Callaway, Phys. Rev. B **15**, 298 (1977); O. Gunnarsson (private communication).
- <sup>26</sup>D. E. Ellis, G. A. Benesh, and E. Byron, Phys. Rev. B **16**, 3308 (1977); J. Appl. Phys. **49**, 1543 (1978).
- <sup>27</sup>W. R. Wampler and B. Lengeler, Phys. Rev. B **15**, 4614 (1977); B. Lengeler, Phys. Rev. B **15**, 5504 (1977).
- <sup>28</sup>R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955); **23**, 1841 (1955).
- <sup>29</sup>D. P. Hutchinson, J. Menes, G. Shapiro, and A. M. Patlach, Phys. Rev. **131**, 1351 (1963).
- <sup>30</sup>L. Hedin, Phys. Rev. **139**, A796 (1965).
- <sup>31</sup>V. G. Grebinnik, I. I. Gurevich, V. A. Zhukov, I. G. Ivanter, A. P. Manych, B. A. Nikol'skii, V. I. Selivanov, and V. A. Sultin, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 11 (1976) [Sov. Phys. JETP Lett. **23**, 8 (1976)].
- <sup>32</sup>R. Yamada, N. Watanabe, K. Sato, H. Asano, and M. Hirabayashi, J. Phys. Soc. Jpn. **41**, 85 (1976); L. A. de-Graaf, J. J. Rush, H. E. Flotow, and J. M. Rowe, J. Chem. Phys. **56**, 4574 (1972); W. Gissler, G. Aledfeld, and T. Springer, J. Phys. Chem. Solids **31**, 2361 (1970).
- <sup>33</sup>J. Bergsma and J. A. Goldkoop, Physica (Utrecht) **26**, 744 (1960).
- <sup>34</sup>J. C. Slater, *The Selfconsistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.