Electronic band and bound-state contributions to the chemical H-H and H-impurity binding

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Abstract. The electronic contributions to the binding energy between a pair of hydrogen atoms and the interaction of hydrogen with transition-metal impurities are estimated in the tight-binding approximation. The role of the band and bound states on the electronic structure of the impurity problem and the pair interactions is examined. The appearance of a bound state below the conduction band contributes noticeably to the chemical interactions. The binding energy between two hydrogen atoms is found to be attractive for the first nearest neighbours. The interaction between hydrogen and transition-metal impurities to the left of Pd in the periodic table is also calculated. In addition to the above, pair interactions between '4d'-type impurities have been estimated.

1. Introduction

The properties of transition metal–hydrogen systems have drawn the attention of researchers working in both applied and fundamental fields of physics and materials science. Actual research projects cover a wide area of topics such as metal hydrogen bonding, the influence of hydrogen on physical and chemical properties, surface studies, diffusion of hydrogen in metals, trapping of hydrogen by defects, etc (Ponyatovesky *et al* 1984, Wicke *et al* 1978, Sakamoto *et al* 1988).

Pröbst and Wagner (1987) recently studied the hydrogen distribution near iron and cobalt solute in palladium hydrides. Their experimental findings agreed with the calculations of Khan *et al* (1981) and Demangeat *et al* (1980) based on a tight-binding description of the Green function method. Unfortunately, these calculations were based on a local neutrality criterion for the change occurring at the impurity site. Needless to say the above approximation is non-self-consistent as indicated in a more elaborate work on the electronic structure of H in Pd (Khalifeh and Demangeat 1983). A hydrogen-induced bound state appears below the Pd conduction band. Owing to this modification, the calculations reported by Khan *et al* have been modified.

A fundamental understanding of the physical phenomena related to trapping of hydrogen by lattice defects in metals remains a challenging problem in the hydrogen–metal system. The introduction of substitutional impurities perturbs the electronic structure of the host and induces strain fields around the impurity. The problem becomes more complicated if hydrogen is added to the system.

Jena *et al* (1985) and Manninen *et al* (1984) have carried out an *ab initio* calculation on the role of the transition metals in hydrogen trapping. In their approach the hydrogen potential energy is constructed in terms of the host electron density map using the effective-medium theory. They include the hydrogen zero-point motion by solving the Schrödinger equation and calculate the hydrogen-induced lattice distortions by using Green function techniques.

Recently, the hydrogen–hydrogen (H–H) and hydrogen–transition-metal impurity (H–T) interactions in FCC ferromagnetic nickel host have been studied by Khalifeh (1988a, b). It has been found that H repels H for the first and second nearest-neighbour positions; whereas in the case of H–'d'-type impurity, hydrogen favours trapping by transition-metal impurities to the left of Ni in the periodic table. Further, the problem of H–H and H–T in vanadium (V) and niobium (Nb) has been studied by Mokrani (1988).

The purpose of this work is to study the electronic structure of Pd and Pd dilute alloys at low hydrogen concentration (α-PdH) at 0 K. The outline of this paper is as follows. Section 2 is devoted to the general formulation of the electronic contribution to the binding energy between two impurities. Section 3 presents the numerical calculations and discussion of the pair interactions in a palladium host. Finally, in § 4 we conclude our work.

2. General formulation

In this section we present a detailed derivation for the electronic part of the binding energy between pairs of impurities such as H–H, H–T and T–T in a Pd host. The following treatment is, in principle, valid for any transition-metal host irrespective of its geometry. However, in the next section our calculations are adapted to an FCC paramagnetic metal. To determine the electronic binding energy we have to start with the electronic structure of isolated impurities (i.e. hydrogen and '4d'-type transition-metal impurities).

2.1. One interstitial impurity

Experimental and theoretical results on the hydrogen–metal systems by Fukai (1984) and Lengler (1984) concerning the lattice site occupancy show that hydrogen occupies octahedral positions (O) in FCC structures for low hydrogen concentrations and tetrahedral positions (T) for high concentrations, whereas in the BCC structure hydrogen atoms occupy tetrahedral sites.

The Hamiltonian of the system, irrespective of the hydrogen position in the host, is given by

$$H = H^0 + |\lambda s\rangle E_\lambda^s \langle \lambda s| + V_\lambda + V' \tag{2.1}$$

where the unperturbed Hamiltonian H^0 is the tight-binding Hamiltonian for the pure metal. Here E_λ^s is the energy level introduced by the isolated interstitial. The term V_λ couples the interstitial atom at λ to the crystal sites R; it has the form

$$V_\lambda = \sum_{R \neq \lambda} |\lambda s\rangle \beta_{\lambda R}^{sm} \langle Rm| + \text{CC} \tag{2.2}$$

where $\beta_{\lambda R}^{sm}$ is the hopping integral between the orbitals of the host and the interstitial at

position λ; m is the orbital symmetry with $m = (s, p, d)$. Here V' represents the variation of the host energy levels due to alloying. It may be stated as

$$V' = \sum_{R,d} |Rd\rangle V_R^d \langle Rd| \tag{2.3}$$

where V_R^d is the variation of the potential induced at the host site R arising from the presence of the interstitial impurity.

To find the potential resulting from the presence of a hydrogen impurity at site λ and the energy level for the isolated atom E_λ^s, we have to solve two non-linear equations. The first equation is

$$2Z_\lambda(\varepsilon_F) = 1 \tag{2.4}$$

where $Z_\lambda(\varepsilon)$ is the number of displaced states up to ε; here the factor 2 accounts for the spin degeneracy, and ε_F is the Fermi energy. The second equation is (Anderson 1961)

$$E_\lambda^s = E_\lambda^{at} + \alpha_\lambda + U_\lambda^{ss} N^s(\lambda) \tag{2.5}$$

where E_λ^{at} is the atomic level of the hydrogen atom in its ground state; α_λ is the variation of the impurity energy level due to its existence in the metal. Here U_λ^{ss} is the Coulomb correlation term in the hydrogen orbitals; $N^s(\lambda)$ is the total number of 's' electrons at the hydrogen site λ. The details of the formalism concerning the interstitial problem are reported in previous papers (Khalifeh and Demangeat 1983, Badirkhan and Khalifeh 1987).

2.2. One '4d'-type impurity

A localised potential approximation is used here in order to describe the modification of the electronic structure of the pure metal due to substitutional impurities (Leonard and Stefanou 1985). The Hamiltonian of the dilute alloy (PdT) is given by

$$H = H^0 + \Delta V_{R_T}. \tag{2.6}$$

Here ΔV_{R_T} is an operator, which takes the form

$$\Delta V_{R_T} = \sum_m |R_T m\rangle \delta V_{R_T} \langle R_T m| \tag{2.7}$$

and δV_{R_T} is the localised potential arising from the replacement of the host atom at site R_T by a new transition-metal impurity having a level δV_{R_T} higher than the common level of the host atoms. The phase shift, $\Delta Z(\varepsilon_F)$, at the Fermi level is written as

$$\Delta Z(\varepsilon_F) = -(1/\pi) \text{Tr arg}[1 - G^0(\varepsilon_F) \delta V_{R_T}]. \tag{2.8}$$

Equation (2.8) is known as Friedel's sum rule; $\Delta Z(\varepsilon_F)$ is the difference in the number of conduction electrons between the substitutional impurity and the host. Once the electronic structure of the single interstitial and substitutional has been performed, one can estimate the binding energy of a pair of impurities.

2.3. Hydrogen–hydrogen binding energy

This section is devoted to the derivation of the electronic binding energy of a pair of interstitials located at the first, second, third and fourth nearest-neighbour octahedral

positions. The Hamiltonian of the system, corresponding to N metallic sites plus two hydrogen interstitials at sites λ and μ, is defined as

$$H = H^{\mathrm{II}} + V_\lambda + V^{\mathrm{nd}}_{\lambda\mu} + V' \tag{2.9}$$

with

$$H^{\mathrm{II}} = H^0 + |\lambda \mathrm{s}\rangle E^{\mathrm{s}}_\lambda \langle \lambda \mathrm{s}| + |\mu \mathrm{s}\rangle E^{\mathrm{s}}_\mu \langle \mu \mathrm{s}|. \tag{2.10}$$

The terms V_λ and V' are defined in § 2.1. Here $V^{\mathrm{nd}}_{\lambda\mu}$ is a direct interaction defined in terms of hopping integrals between the 's' orbitals of the interstitials

$$V^{\mathrm{nd}}_{\lambda\mu} = |\lambda \mathrm{s}\rangle \beta^{\mathrm{ss}}_{\lambda\mu} \langle \mu \mathrm{s}| + \mathrm{CC}. \tag{2.11}$$

The chemical binding energy between a pair of interstitial impurities takes the form (Demangeat *et al* 1980).

$$\Delta E(\lambda, \mu) = -\int_{-\infty}^{\varepsilon_{\mathrm{F}}} [Z_{\lambda\mu}(\varepsilon) - Z_\lambda(\varepsilon) - Z_\mu(\varepsilon)] \, \mathrm{d}\varepsilon. \tag{2.12}$$

Here $Z_{\lambda\mu}(\varepsilon)$ is the phase shift corresponding to a pair of hydrogen atoms at the octahedral sites λ and μ.

The pair interaction can be separated into two terms: the band contribution, which is given by the integral from ε_{b} up to ε_{F}, and the bound-states contribution, due to the poles of the expression. In the present case for $\varepsilon < \varepsilon_{\mathrm{b}}$, the poles lie outside the conduction band. The final form of the H–H binding energy becomes (Shadid 1989)

$$\Delta E(\lambda, \mu) = 2(E_1 + E_2 - 2E_0) + \frac{2}{\pi} \int_{\varepsilon_{\mathrm{b}}}^{\varepsilon_{\mathrm{F}}} \arg[1 - F(\varepsilon)] \, \mathrm{d}\varepsilon \tag{2.13}$$

where $F(\varepsilon)$ is written as

$$F(\varepsilon) = \frac{[\Delta^{\mathrm{ss}}_{\lambda\mu}(\varepsilon) + \Gamma^{\mathrm{ss}}_{\lambda\mu}(\varepsilon) + \beta^{\mathrm{ss}}_{\lambda\mu}][\Delta^{\mathrm{ss}}_{\mu\lambda}(\varepsilon) + \Gamma^{\mathrm{ss}}_{\mu\lambda}(\varepsilon) + \beta^{\mathrm{ss}}_{\mu\lambda}]}{[\varepsilon - E^{\mathrm{s}}_\lambda - \Delta^{\mathrm{ss}}_{\lambda\lambda}(\varepsilon) - \Gamma^{\mathrm{ss}}_{\lambda\lambda}(\varepsilon)][\varepsilon - E^{\mathrm{s}}_\lambda - \Delta^{\mathrm{ss}}_{\mu\mu}(\varepsilon) - \Gamma^{\mathrm{ss}}_{\mu\mu}(\varepsilon)]} \tag{2.14}$$

2.4. Hydrogen–'4d'-type impurity binding energy

In this section, we derive the chemical binding energy between a hydrogen interstitial located at an octahedral site and a '4d'-type transition-metal impurity located at the first and second substitutional neighbouring positions. Let the hydrogen atom be located at site λ $(0, 0, 0)$ and the '4d'-type transition-metal impurity be located at R_{T}. Then, the Hamiltonian of the dilute alloy will have the form

$$H = H^0 + |\lambda \mathrm{s}\rangle E^{\mathrm{s}}_\lambda \langle \lambda \mathrm{s}| + V_\lambda + \Delta V_{R_{\mathrm{T}}} + V' \tag{2.15}$$

where quantities V_λ, $\Delta V_{R_{\mathrm{T}}}$ and V' on the right-hand side of the above equation are already given in equations (2.2), (2.7) and (2.3), respectively. The chemical binding energy has a form similar to that of equation (2.12) (Khalifeh 1982)

$$\Delta E(\lambda, R_{\mathrm{T}}) = -\int_{-\infty}^{\varepsilon_{\mathrm{F}}} [Z_{\lambda R_{\mathrm{T}}}(\varepsilon) - Z_\lambda(\varepsilon) - \Delta Z_{R_{\mathrm{T}}}(\varepsilon)] \, \mathrm{d}\varepsilon. \tag{2.16}$$

Here $Z_{\lambda R_{\mathrm{T}}}(\varepsilon)$ is the phase shift corresponding to hydrogen and '4d'-type impurities.

The final form of binding energy including the bound-states contribution is written as

$$\Delta E(\lambda, R_\mathrm{T}) = 2(E_1 - E_0)$$

$$+ \frac{2}{\pi} \int_{\varepsilon_\mathrm{b}}^{\varepsilon_\mathrm{F}} \arg\left(1 - \frac{\chi_{\lambda\lambda}^{\mathrm{ss}}(\varepsilon) + 2L_{\lambda\lambda}^{\mathrm{ss}}(\varepsilon)}{[\varepsilon - E_\lambda^\mathrm{s} - \Delta_{\lambda\lambda}^{\mathrm{ss}}(\varepsilon) - \Gamma_{\lambda\lambda}^{\mathrm{ss}}(\varepsilon)]}\right) \mathrm{d}\varepsilon \tag{2.17}$$

where E_1 and E_0 are the positions of the bound states before and after the alloying. The above quantities are defined in the Appendix.

2.5. '4d'–'4d'-type impurity binding energy

In this section, we are interested in estimating the binding energy between two '4d' substitutional impurities of the '4d' transition-metal series in palladium. The Hamiltonian is given by

$$H = H^0 + \Delta V_{R_1} + \Delta V_{R_2} \tag{2.18}$$

where ΔV_{R_1} and ΔV_{R_2} are the potentials arising from the presence of the substitutionals at sites R_1 and R_2, respectively. By using Dyson's equation, the Green function matrix elements can be obtained. Here, $Z_{R_1 R_2}(\varepsilon)$ is the number of displaced states after alloying. So that

$$\Delta E(R_1, R_2) = \frac{2}{\pi} \int_{-\infty}^{\varepsilon_\mathrm{F}} \arg\left(1 - \sum_\mathrm{d} G_{R_1 R_2}^{0\mathrm{d}}(\varepsilon)\Delta t_{R_2} G_{R_2 R_1}^{0\mathrm{d}}(\varepsilon)\Delta t_{R_1}\right) \mathrm{d}\varepsilon. \tag{2.19}$$

This formula is valid for the calculation of the binding energy between two substitutional impurities separated by a distance $|R_1 - R_2|$ and for different distances with different transition-metal impurities.

3. Numerical results and discussion

3.1. Introduction

The aim of this section is to summarise the calculations of the pair interactions according to the formulation presented in the previous section. The electronic structure of pure palladium is described in terms of a tight-binding Hamiltonian with a Slater–Koster linear combination of atomic orbitals (SK–LCAO) in terms of two-centre integrals and an orthogonal basis set. The SK parameters used here are obtained by fitting the results of the first-principles augmented plane-wave band-structure calculation to an LCAO basis (Papaconstantopoulos 1986).

It is convenient to sketch the local density of states (LDOS) for Pd (figure 1). The integrated 's'- and 'p'-type density of states gives a small contribution to the total density of states, whereas the largest contribution, as expected, is due to the 'd' band.

3.2. Electronic structure of one interstitial impurity

In this section, numerical values of E_λ^s and V^d are found by solving equations (2.4) and (2.5) self-consistently for different values of the Coulomb integral, which varies in the
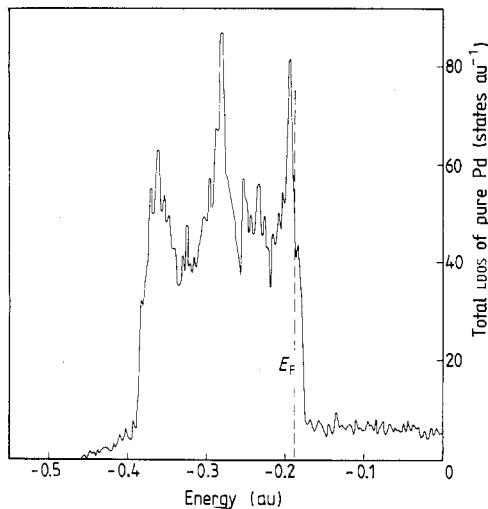
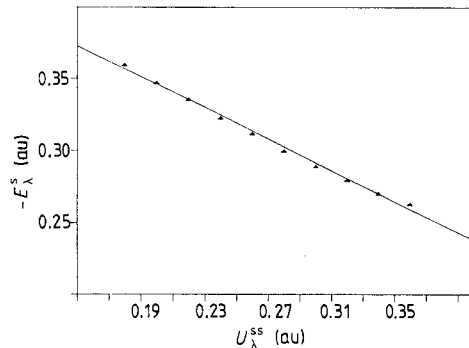**Figure 1.** Total local density of states of pure palladium.

Figure 2. Effective energy level $-E_\lambda^s$ versus Coulomb integral U_λ^{ss}.

Table 1. Hopping integrals (Ryd) between 's' orbital and metallic 's', 'p' and 'd' orbitals.

$ss\sigma$	$sp\sigma$	$sd\sigma$
0.087	0.162	0.120

range 0.18 to 0.36 au. Bear in mind that the value of E_λ^{at} is equal to -1 Ryd for the hydrogen atom in its ground state (i.e. $E_\lambda^{at} = -0.5$ au). The crystal field α_λ is neglected (Darby *et al* 1981). The total number of electrons at the hydrogen site is due to two contributions: the first is due to the filling of the bound state whereas the second arises from the conduction band. Similarly, the variation of the LDOS at the metallic site is also given as a sum of two terms. Our calculations for different values of U_λ^{ss} show that a charge transfer occurs from metal sites to the hydrogen impurity. Furthermore, the existence of the bound state below the conduction band is in agreement with other calculations (Khalifeh and Demangeat 1983); the latter's work includes the diagonal elements of Green functions only. Our results also agree with a different technique using a self-consistent muffin-tin Green function method (Yussouff and Zeller 1981). The total number of electrons in the zone of the first nearest neighbours of the hydrogen is different from the number of electrons at the impurity site, which means that other terms should be included in the Hamiltonian.

Figure 2 represents a relationship between the effective energy level E_λ^s and the Coulomb integral U_λ^{ss}. The graph can approximately be represented by a straight line, which means that the dependence of the energy level on the integrated LDOS at the hydrogen site is negligible. The hopping integrals between the hydrogen 's' orbital and the 's', 'p' and 'd' orbitals for the metallic sites (Pd) are restricted to the first nearest neighbours of H. The values of these parameters are shown in table 1 (Faulkner 1976).
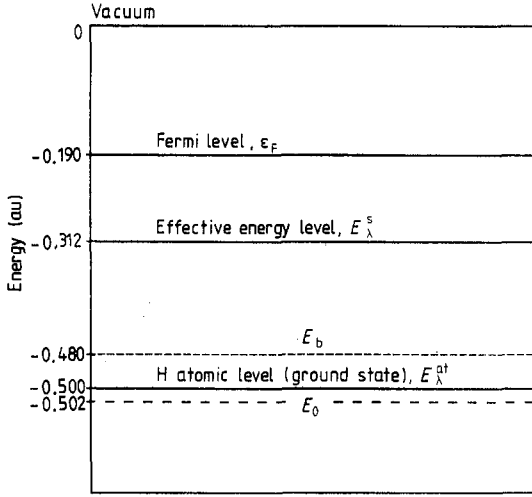
Figure 3. The positions of the Fermi level ε_F, atomic level for the hydrogen atom E_λ^{at} and effective energy level E_λ^s.

In solving equations (2.4) and (2.5) the following approximation is used (Badirkhan 1986):

$$V^d(\Gamma_{12}) = V^d(\Gamma_{25}') \tag{3.1}$$

so that $Z_\lambda(\varepsilon)$ in equation (2.4) becomes

$$Z_\lambda(\varepsilon) = -(1/\pi)\,\arg[\varepsilon - E_\lambda^s - \Delta_{\lambda\lambda}^{ss}(\varepsilon) - \Gamma_{\lambda\lambda}^{ss}(\varepsilon)]$$

$$- 6V^d(\Gamma_{12})[3n^{0d}(\Gamma_{25}') + 2n^{0d}(\Gamma_{12})]. \tag{3.2}$$

Following Khalifeh and Demangeat (1983) the Coulomb integral for the P̲d̲H̲ system is equal to 0.26 au. A solution of our problem for the above-mentioned value gives $V^d = -0.00128$ au and $E_\lambda^s = -0.3118$ au (figure 3). These values are needed in calculating the variation of LDOS at the metallic site R (figure 4) and the LDOS at the hydrogen site (figure 5).

3.3. Electronic structure of one '4d'-type impurity

It is convenient to use a localised potential model for the single substitutional impurity since it makes the treatment of this problem easier than taking all the elements of the potential operator. Therefore, Friedel's sum rule (equation (2.8)) is sufficient to find out the values of the potential introduced by the '4d'-type transition-metal impurities appearing to the left of Pd in the periodic table (i.e. Rh, Ru, Tc, Mo). We neglect the localised potentials for 's' and 'p' and we assume equal values for the localised potentials corresponding to 'd$_{25}'$' and 'd$_{12}$'. Thus equation (2.8) becomes

$$\Delta Z_R(\varepsilon_F) = -(2/\pi)\{3\,\arg[1 - \delta V_d(\Gamma_{12})G^0(\Gamma_{25}')]$$

$$+ 2\,\arg[1 - \delta V_d(\Gamma_{12})G^0(\Gamma_{12})]\}. \tag{3.3}$$

However, other calculations on BCC transition hosts (Mokrani 1988) take the 's' part of the potential into account by imposing $\delta V_d = 2\delta V_s$. Equation (3.3) can be solved self-consistently by iteration. This approach is satisfactory when the number of conduction electrons of the impurity is slightly different from that of the host.
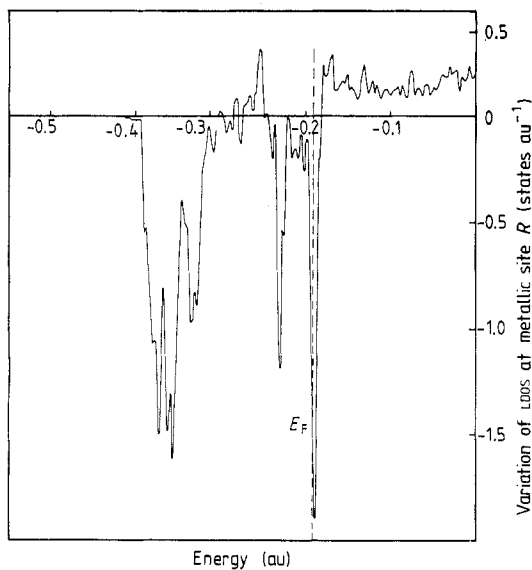
Figure 4. Variation of the density of states at the metallic site R.
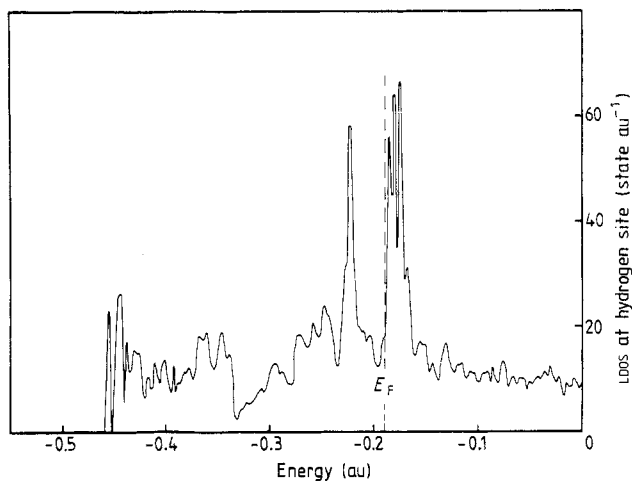

Figure 5. Local density of states at the hydrogen site for $V^d = -0.001\,28$ au and $U_\lambda^{ss} = 0.26$ au.

Table 2 shows an opposite sign behaviour between the charge difference $\Delta Z_R(\varepsilon_F)$ and the localised potential δV_d.

3.4. Estimation of the hydrogen–hydrogen binding energy

In this section, we calculate the electronic contribution to the H–H binding energy.

Table 2. Localised substitutional impurity potential $\delta V_d(\Gamma_{12})$ values (au).

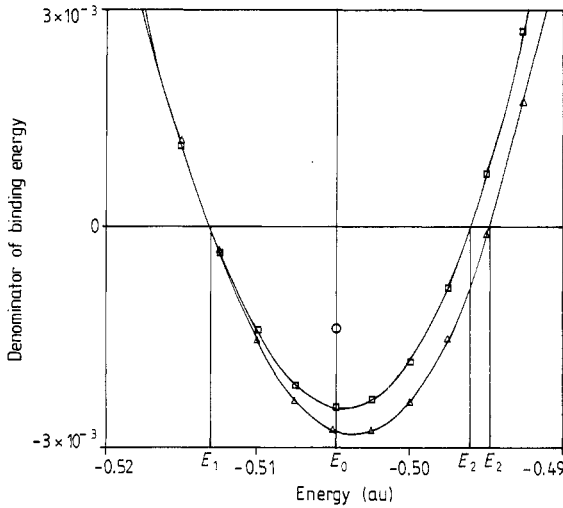| $\Delta Z_R(\varepsilon_F)$	-1 (Rh)	-2 (Ru)	-3 (Tc)	-4 (Mo)
δV_d	0.013	0.023	0.031	0.038

Figure 6. Positions of the bound states: (●) one impurity; (□) two impurities, first nearest neighbours; (▲) two impurities, second nearest neighbours.

First, if the direct hopping integral between the two interstitials is neglected, equation (2.13) becomes

$$\Delta E(\lambda, \mu) = 2(E_1 + E_2 - 2E_0)$$

$$+ \frac{2}{\pi} \int_{\varepsilon_b}^{\varepsilon_F} \arg\left(1 - \frac{[\Delta_{\lambda\mu}^{ss}(\varepsilon) + \Gamma_{\lambda\mu}^{ss}(\varepsilon)]^2}{[\varepsilon - E_\lambda^s - \Delta_{\lambda\lambda}^{ss}(\varepsilon) - \Gamma_{\lambda\lambda}^{ss}(\varepsilon)]^2}\right) d\varepsilon. \qquad (3.4)$$

The above equation gives the indirect interaction between H atoms, where E_1 and E_2 are the positions of the first and second bound states corresponding to the H–H interaction; E_0 is the bound-state position arising from the single interstitial problem (figure 6). All the quantities in equation (3.4) are defined in the Appendix.

To calculate the bound-state contribution to the binding energy (i.e. the first term on the right-hand side of equation (2.13)), a test program is used to check out the singularities of the second part. The calculated exact and asymptotic binding energies for the previous case are shown in table 3. Note that the asymptotic interaction is represented by the leading term in the argument, i.e. $\ln(1 - x) \simeq -x$. We have estimated the third and fourth nearest-neighbour interactions, but their contributions are negligible; hence they are not reported.

Secondly, taking the direct interaction between the interstitials into account, by considering the values of the hopping integrals $\beta_{\lambda\mu_1}^{ss} = 0.0208$ au and $\beta_{\lambda\mu_2}^{ss} = 0.0045$ au furnished by Faulkner (1976), we obtain the results in table 4.

Table 3. Exact and asymptotic binding energies (meV) between two interstitial hydrogen atoms, one at site λ and the other at sites $\mu_1 (1, 1, 0)$ and $\mu_2 (0, 2, 0)$, respectively, when $V^d = -0.001\,28$ and $\beta_{\lambda\mu}^{ss} = 0$.

Form	Bound-state contrib.	Band contrib.		Total binding energy	
		Exact	Asymp.	Exact	Asymp.
$\Delta E(\lambda, \mu_1)$	-15.0	-2.6	-3.0	-17.6	-18.0
$\Delta E(\lambda, \mu_2)$	26.9	-9.8	-9.3	17.1	17.6

Table 4. Exact and asymptotic binding energies (meV) between two interstitial hydrogen atoms, one at site λ and the other at sites μ_1 and μ_2, respectively, when $V^d = -0.001\,28$ and the values of $\beta_{\lambda\mu}^{ss}$ are as given by Faulkner (1976).

Form	Bound-state contrib.	Band contrib.		Total binding energy	
		Exact	Asymp.	Exact	Asymp.
$\Delta E(\lambda, \mu_1)$	-41.0	35.7	34.4	-5.6	-6.9
$\Delta E(\lambda, \mu_2)$	31.0	-14.3	-13.8	26.7	27.2

Table 5. Exact and asymptotic binding energies (meV) between interstitial hydrogen impurity at octahedral site and a '4d' transition-metal impurity in the first nearest neighbour position as a function of $\Delta Z_R(\varepsilon_F)$ (given $V^d = -0.001\,28$).

$\Delta Z_R(\varepsilon_F)$	Bound-state contrib.	Band contrib.		Total binding energy	
		Exact	Asymp.	Exact	Asymp.
-1 (Rh)	6.6	58.9	59.2	65.5	65.8
-2 (Ru)	10.9	103.3	104.6	114.2	115.5
-3 (Tc)	14.0	138.4	140.5	152.4	154.5
-4 (Mo)	16.8	164.1	163.5	180.9	180.3

3.5. Estimation of the hydrogen–'4d'-type impurity binding energy

In this part the binding energy between the hydrogen atom at an octahedral site and a substitutional impurity at the first and second nearest-neighbour locations is calculated according to relation (2.17). We refer back to § 2.4, where the quantities $\chi_{\lambda\lambda}^{ss}(\varepsilon)$ and $L_{\lambda\lambda}^{ss}(\varepsilon)$ are given in the Appendix.

Table 5 displays the binding energy values between hydrogen and transition-metal impurity neighbours to Pd in the periodic table given as a function of $\Delta Z_R(\varepsilon_F)$.

Our results show that, for negative $\Delta Z_R(\varepsilon_F)$, the electronic energy is repulsive for short ranges. The binding energies for H–'d'-type impurities in Pd agree with calculations done by Demangeat *et al* (1980) for $\Delta Z_R(\varepsilon_F) = -2, -3$ and -4, while it is different from
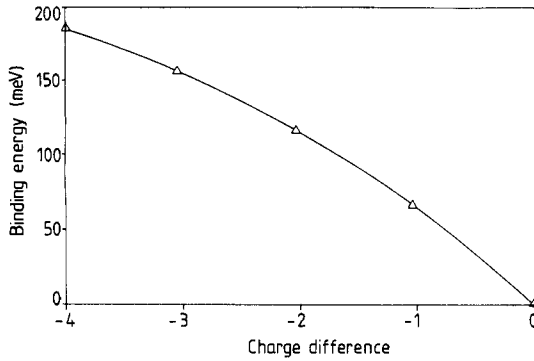
Figure 7. Binding energy (meV) between hydrogen impurity located at site λ and a transition-metal impurity at the first nearest-neighbour position with $\Delta Z_R = -1$, -2, -3 and -4.

Table 6. Exact binding energy (meV) between two substitutional impurities located at the first nearest-neighbour positions.

$\Delta E(R_1, R_2)$	-1 (Rh)	-2 (Ru)	-3 (Tc)	-4 (Mo)
-1 (Rh)	-0.4	-0.9	-1.2	-1.1
-2 (Ru)	-0.9	-1.7	-2.3	-1.6
-3 (Tc)	-1.2	-2.3	-2.9	-0.9
-4 (Mo)	-1.1	-1.6	-0.9	4.9

theirs for $\Delta Z_R(\varepsilon_F) = -1$. The second neighbour interaction H–T is small enough; hence it is neglected (cf figure 7).

3.6. Estimation of the '4d'–'4d'-type impurity binding energy

In § 2.5 we have shown that no singularities are present in the T–T interaction, so that the binding energy is a result of the band contribution only. Thus $\Delta E(R_1, R_2)$ is

$$\Delta E(R_1, R_2) = \frac{2}{\pi} \int_{-\infty}^{\varepsilon_F} \arg[1 - T^d_{R_1R_2}(\varepsilon)] \, d\varepsilon \tag{3.5}$$

where

$$T^d_{R_1R_2}(\varepsilon) = \Delta t^{d1}_{R1} \Delta t^{d1}_{R2} [G^0(1)^2 + 2G^0(2)]$$
$$+ \Delta t^{d4}_{R_1} \Delta t^{d4}_{R_2} \tfrac{1}{9}\{[G^0(4) - 4G^0(5)]^2 + G^0(4)^2\} \tag{3.6}$$

and

$$\Delta t^{d1}_{R_1} = \delta V_{R_1}/[1 - \delta V_{R_2} G^0(\Gamma'_{25})] \tag{3.7}$$

$$\Delta t^{d4}_{R_2} = \delta V_{R_2}/[1 - \delta V_{R_2} G^0(\Gamma_{12})]. \tag{3.8}$$

Table 6 shows the numerical results of the T–T binding, which are calculated in terms of the screening potential values listed in table 2.
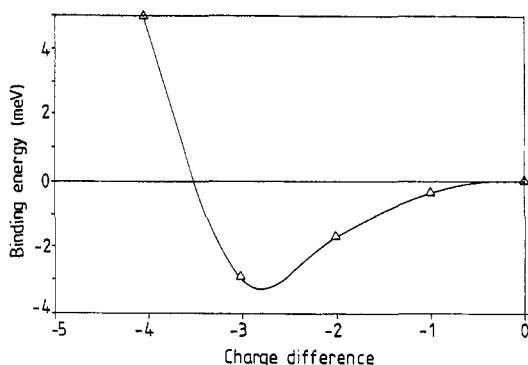
Figure 8. Binding energy (meV) between two identical transition-metal impurities.

4. Conclusions

In this work we have investigated the electronic structure resulting from the introduction of a hydrogen or a transition-metal impurity in FCC paramagnetic palladium. We have carried out a detailed calculation of the binding energy between pairs of hydrogen–hydrogen and between hydrogen–transition-metal impurity and the interaction between transition-metal impurities in Pd. A single extra orbital for the interstitial problem, a localised potential for the case of a substitutional impurity and a double extra orbital for the hydrogen–hydrogen interactions are used in this paper.

The main features of our attempt are as follows:

Bound states are present below the conduction band for the interstitial problem, the hydrogen–hydrogen and the hydrogen–transition-metal impurity interactions.

The bound-states contribution to the hydrogen–hydrogen interaction is more important than that of the band, whereas the bound-states contribution is less for the hydrogen–'4d'-type impurity compared with that of the band (tables 4 and 5).

An attractive H–H interaction is observed for the first nearest-neighbour position. This behaviour might be related to neglect of the short-range repulsive Coulomb interaction. On the other hand, the elastic contribution to the H–H has been previously calculated by Khalifeh *et al* (1983) and found to be of the same order of magnitude as that of the electronic term.

Transition-metal impurities of the '4d' type lying to the left of Pd in the periodic table repel hydrogen (table 5 and figure 8). A clear and final statement about the trapping procedure is still not available because the elastic contribution to the trapping energy is not yet determined. However, Jena *et al* (1985) recently considered the trapping of hydrogen to be governed by the elastic interaction.

In a recent work, Mokrani and Demangeat (1989) have considered the electron–electron interaction in their investigation of the hydrogen impurity problem in V and Nb. Our future objective is to extend this work on the FCC host so as to include the above-mentioned term. It is worth mentioning that such a calculation can cover other cubic transition metals if the electronic structure of hydrogen in these metals is obtained, which is, unfortunately, not the case for most of the three series of transition metals in the periodic table.

Appendix

The aim of this appendix is to calculate some terms appearing in this text. Here we have the values of $\Delta_{\lambda\lambda}^{\text{ss}}(\varepsilon)$ and $\Gamma_{\lambda\lambda}^{\text{ss}}(\varepsilon)$:

$$\Delta_{\lambda\lambda}^{\text{ss}}(\varepsilon) = 6[(\text{ss}\sigma)^2 G^0(\Gamma_1) + (\text{sp}\sigma)^2 G^0(\Gamma_{15}) + (\text{sd}\sigma)^2 G^0(\Gamma_{12})] + 24(\text{sd}\sigma)^2 G^0(7)$$
$$+ 60(\text{ss}\sigma)(\text{sd}\sigma)G^0(9) + 12(\text{sd}\sigma)^2[G^0(4) - G^0(5)] \tag{A1}$$

and

$$\Gamma_{\lambda\lambda}^{\text{ss}}(\varepsilon) = V^{\text{d}}\{96[(\text{ss}\sigma)G^0(9)]^2 + 96[(\text{sd}\sigma)G^0(\Gamma_{12})]^2 + 24(\text{sd}\sigma)^2[G^0(4)^2 - 4G^0(5)^2]$$
$$+ 48(\text{ss}\sigma)(\text{sd}\sigma)G^0(9)G^0(4) + 24(\text{ss}\sigma)^2 G^0(9)[G^0(4) - 2G^0(5)]$$
$$+ 96(\text{ss}\sigma)(\text{sd}\sigma)G^0(9)[G^0(4) - 2G^0(5)] - 96(\text{sd}\sigma)^2 G^0(4)G^0(5)\} \tag{A2}$$

where $G^0(\Gamma_1)$, $G^0(\Gamma_{15})$, $G^0(\Gamma_{12})$ and $G^0(\Gamma_{25}')$ are the intra-site Green function matrix elements for 's', 'p', '$\text{d}_{x^2-y^2}$' and 'd_{xy}', respectively; $G^0(1)$, $G^0(2), \ldots, G^0(9)$ are the inter-site Green functions. The values of $\Delta_{\lambda\mu}^{\text{ss}}(\varepsilon)$ and $\Gamma_{\lambda\mu}^{\text{ss}}(\varepsilon)$ are

$$\Delta_{\lambda\mu 1}^{\text{ss}}(\varepsilon) = (\text{ss}\sigma)^2[16G^0(7) + 2G^0(\Gamma_1)] - 4(\text{ss}\sigma)(\text{sd}\sigma)G^0(9)$$
$$- (\text{sd}\sigma)^2[G^0(\Gamma_{12}) + 2G^0(4) - 6G^0(5)] \tag{A3}$$
$$\Delta_{\lambda\mu 2}^{\text{ss}}(\varepsilon) = (\text{ss}\sigma)^2[8G^0(7) + G^0(\Gamma_1)] + 16(\text{ss}\sigma)(\text{sd}\sigma)G^0(9)$$
$$+ (\text{sd}\sigma)^2[G^0(\Gamma_{12}) + 2G^0(4) - 6G^0(5)] \tag{A4}$$

and

$$\Gamma_{\lambda\mu 1}^{\text{ss}}(\varepsilon) = V^{\text{d}}\{-8[(\text{ss}\sigma)G^0(9)]^2 + (\text{sd}\sigma)^2[-G^0(\Gamma_{12})^2 - 2G^0(4)^2 - 8G^0(5)^2$$
$$- 24G^0(4)G^0(5) + G^0(\Gamma_{12})(-3G^0(4) + 10G^0(5))]$$
$$+ (\text{ss}\sigma)(\text{sd}\sigma)G^0(9)[-6G^0(\Gamma_{12}) - 8G^0(4) + 16G^0(5)]\} \tag{A5}$$
$$\Gamma_{\lambda\mu 2}^{\text{ss}}(\varepsilon) = V^{\text{d}}\{32[(\text{ss}\sigma)G^0(9)]^2 + (\text{sd}\sigma)^2[G^0(\Gamma_{12})^2 + 9G^0(4)^2 + 32G^0(5)^2$$
$$- 34G^0(4)G^0(5) + G^0(\Gamma_{12})(\tfrac{13}{2} G^0(4) - 12G^0(5))]$$
$$+ (\text{ss}\sigma)(\text{sd}\sigma)G^0(9)[12G^0(\Gamma_{12}) + 26G^0(4) - 48G^0(5)]\}. \tag{A6}$$

The quantity $Z_{\lambda R_{\text{T}}}(\varepsilon)$ appearing in equation (2.16) is given by

$$Z_{\lambda R_{\text{T}}}(\varepsilon) = -\frac{1}{\pi} \arg[K(\varepsilon)] - \sum_{\text{d}} G^{0\text{d}}(\varepsilon) \Delta t_{R_{\text{T}}}^{\text{d}}(\varepsilon) \tag{A7}$$

and

$$K(\varepsilon) = \varepsilon - E_\lambda^{\text{s}} - \Delta_{\lambda\lambda}^{\text{ss}}(\varepsilon) - \Gamma_{\lambda\lambda}^{\text{ss}}(\varepsilon) - \chi_{\lambda\lambda}^{\text{ss}}(\varepsilon) - 2L_{\lambda\lambda}^{\text{ss}}(\varepsilon) \tag{A8}$$

with

$$\chi_{\lambda\lambda}^{\text{ss}}(\varepsilon) = \sum_{\substack{m',\text{d},\zeta, \\ \rho,\eta}} \beta_{\lambda\rho}^{sm'} G_{\rho R_{\text{T}}}^{m'\text{d}}(\varepsilon) \Delta t_{R_{\text{T}}}^{\text{d}} G_{R_{\text{T}}\zeta}^{\text{d}\eta}(\varepsilon) \beta_{\zeta\lambda}^{\eta s} \tag{A9}$$

$$L_{\lambda\lambda}^{\text{ss}}(\varepsilon) = \sum_{\substack{m',\zeta,n, \\ \rho,\eta,\nu,\text{d}}} \beta_{\lambda\rho}^{sm'} G_{\rho R_{\text{T}}}^{m'\text{d}} \Delta t_{R_{\text{T}}}^{\text{d}} G_{R_{\text{T}}\zeta}^{\text{dd}}(\varepsilon) V^{\text{d}} G_{\zeta\nu}^{\text{d}n}(\varepsilon) \beta_{\nu\lambda}^{ns} \tag{A10}$$

and

$$\Delta t_{R_{\text{T}}}(\varepsilon) = \delta V_{R_{\text{T}}}\left(1 - \delta V_{R_{\text{T}}} G^{0\text{d}}(\varepsilon) - \sum_{\rho,\text{d}} G_{R_{\text{T}}\rho}^{0\text{dd}}(\varepsilon)\delta V_{R_{\text{T}}}V^{\text{d}}\right)^{-1}. \tag{A11}$$

When the substitutional impurity is located at R_1, we have

$$\chi_{\lambda\lambda}^{\text{ss}}(\varepsilon)_{R_1} = (A_3^{\text{d}5})^2(3\Delta t_{R_1}^{\text{d}4} + \Delta t_{R_1}^{\text{d}5}) \tag{A12}$$

where

$$A_3^{d5} = -2(ss\sigma)G^0(9) - \tfrac{1}{2}(sd\sigma)[G^0(\Gamma_{12}) + 2G^0(4) - 4G^0(5)] \tag{A13}$$

and

$$\Delta t_{R_1}^{d4} = \delta V_{R_1}/\{1 - G^0(\Gamma_{12})\delta V_{R_1} - \delta V_{R_1}V^d[2(G^0(4) - 4G^0(5))^2/9$$
$$+ 2(-2G^0(4) + G^0(5))^2/9 + G^0(\Gamma_{12})^2]\} \tag{A14}$$

$$\Delta t_{R_1}^{d5} = \delta V_{R_1}/\{1 - G^0(\Gamma_{12})\delta V_{R_1}$$
$$- \delta V_{R_1}V^d[2G^0(4)^2 + 2G^0(5)^2 + G^0(\Gamma_{12})^2]\}. \tag{A15}$$

Similarly, the summation in equation (A10) leads to the expression

$$L_{\lambda\lambda}^{ss}(\varepsilon)_{R_1} = 9\delta V_{R_1}V^d[2(sd\sigma)^2 G^0(6) - (ss\sigma)(sd\sigma)G^0(6)G^0(8)$$
$$+ (ss\sigma)^2 G^0(8)^2][G^0(2) + G^0(3)]. \tag{A16}$$

The phase shift corresponding to two substitutional '4d'-type impurities is

$$Z_{R_1R_2}(\varepsilon) = -(2/\pi)\{\arg[1 - G^{0d}(\varepsilon)\delta V_{R_1}] + \arg[1 - G^{0d}(\varepsilon)\delta V_{R_2}]$$
$$- G_{R_1R_2}^{0d}(\varepsilon)\Delta t_{R_2}G_{R_2R_1}^{0d}(\varepsilon)\delta V_{R_1}\}. \tag{A17}$$

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