Journal of the Less-Common Metals, 172–174 (1991) 1371–1380

Interaction between two neighboring deuterium atoms in palladium

Ken-ichi Tsuchiya
Department of Electronic Engineering, Tokyo National College of Technology, Kunugida, Hachioji, Tokyo 193 (Japan)

Yoshiko H. Ohashi
Department of Instrumentation Engineering, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama, Kanagawa 223 (Japan)

Kazutoshi Ohashi
Faculty of Engineering, Tamagawa University, Machida, Tokyo 194 (Japan)

Mitsuru Fukuchi
Department of Instrumentation Engineering, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama, Kanagawa 223 (Japan)

Abstract

In this work, the nearest neighbor distance between two deuterium atoms in an f.c.c. palladium lattice was estimated by taking into account the effect of an electronic screening cloud. The lattice was assumed to contain a deuterium atom at the nearest neighbor octahederal site to a vacancy, and the potential energy field experienced by another deuterium atom was constructed by a pair potential technique. In this resulting field, the Schrödinger equation for another deuterium atom was solved, and the distance between two neighboring deuterium atoms was estimated. Our result for the distance was about 0.66 Å, which is smaller than the molecular value of 0.74 Å.

1. Introduction

Recently, many workers have shown considerable interest in the deuterium atoms in palladium, because it is suggested that they are related to cold nuclear fusion [1, 2]. The theoretical interest in this problem is the nearest neighbor distance between deuterium atoms, since the probability of the deuterium fusion reaction being induced by a tunneling effect crucially depends on it. There are three points to this problem. Firstly, deuterium atoms produce strong perturbation of the conduction electrons and induce an electronic screening cloud. Secondly, the deuterium atoms are so light that they act as quantum particles. Thirdly, the deuterium atoms need enough space in the lattice to be able to approach each other. Considering these points, we have studied deuterium atoms in palladium and estimated the nearest neighbor distance between them.

We considered the interactions between a deuterium atom and the host lattice when the deuterium is embedded in the host f.c.c. palladium lattice

0022-5088/91/$3.50

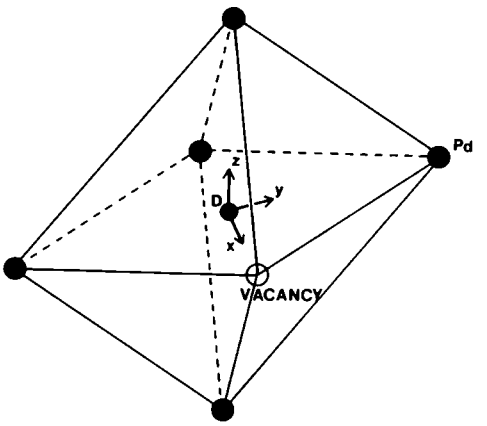

Fig. 1. The f.c.c. palladium lattice containg a deuterium atom at the nearest neighbor O site from a vacancy.

which contains a deuterium atom at the nearest neighbor octahederal (O) site from a vacancy, as illustrated in Fig. 1. In this host lattice, the vacancy supplies enough space for the embedded deuterium atom to exist at the vicinity of included deuterium. The behavior of embedded deuterium as a quantum particle is described by the solution of the Schrödinger equation. In this equation, the potential energy field experienced by embedded deuterium is described by pair-wise interaction between D–D and D–Pd atoms. The pair potential between embedded deuterium and included deuterium is evaluated from the direct coulomb interaction and the non-linear screening effect term [3–5] which cancel the direct term. The screening effect considered here is the usual effect from normal electrons, while Jones *et al.* [2] suggested a screening effect associated with quasiparticles of large effective mass. The pair potential between the embedded deuterium and host palladium atoms is constructed using Pettifor's pseudopotential for 4d-transition metals [6, 7], in which it is assumed that the 4d electrons move rigidly with the ion.

2. D–D pair potential

We construct the D–D pair potential V_{D-D} by applying density functional theory to a system in which two deuterium atoms are embedded in jellium at positions $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. The charge distribution around two deuterium atoms is approximated by overlapping the two electron densities. Each of them can be calculated using the Kohn–Sham method [3], which includes the parameter r_s. The Wigner–Seitz radius r_s for Pd($4d^{10}5s^0$) is determined from free electron-like s-band occupancy N_s and atomic volume V by $\frac{4}{3}\pi r_s^3 = V/N_s$. We calculated the self-consistent charge density distribution and effective potential around a deuterium atom in palladium jellium of $r_s = 3.05$ u which is determined from $N_s = 0.84$ [6]. The induced charge $\Delta n(r)$, plotted in Fig. 2,

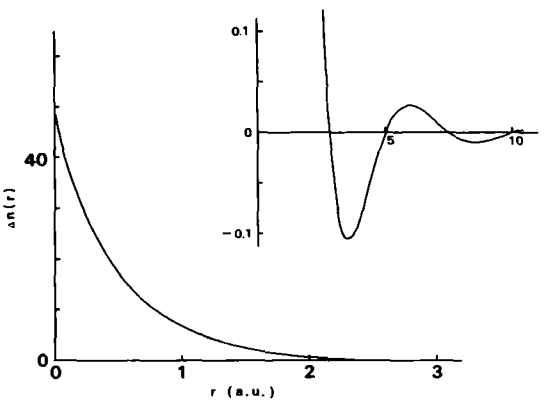

Fig. 2. Deviation of electron density around a deuterium atom in palladium jellium from the mean density n_0, normalized by n_0.

plays an important role in the interaction between two deuterium atoms, because it cancels the direct coulomb interaction. The self-consistent effective potential $V_{\text{eff}}(r)$ for electrons around the deuterium atom is written as

$$V_{\text{eff}}(r) = \phi_{\text{s}}(r) + \phi_{\text{xc}}(r) \tag{1}$$

where ϕ_{s} and ϕ_{xc} are electrostatic and exchange-correlation potentials respectively, and the results are plotted in Fig. 3. The electrostatic term is divided into the direct coulomb interaction and electron-induced potential $v_{\text{s}}(r)$ as

$$\phi_{\text{s}}(r) = -\frac{2}{r} + v_{\text{s}}(r) \tag{2}$$

In eqn. (2), the factor 2 of the first term on the right-hand side is caused by using the Rydberg unit, which is used throughout this paper.

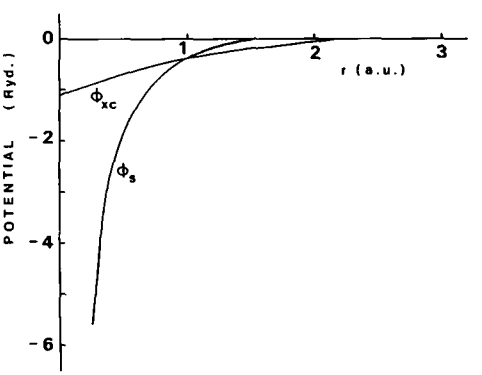

Fig. 3. Electrostatic ϕ_{s} and exchange-correlation ϕ_{xc} potential experienced by electrons around a deuterium atom.

The change in energy due to the embedding of the two deuterium atoms is divided into electrostatic, exchange-correlation and kinetic contributions. The change in electrostatic energy is written as

$$\Delta E_{es}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{2}\sum_{i \neq j} \int\int \mathrm{d}\boldsymbol{r}\ \mathrm{d}\boldsymbol{r}' \frac{2\Delta\rho_i(\boldsymbol{r})\ \Delta\rho_j(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{3}$$

where the summation is run over the two atoms and $\Delta\rho_i$ is defined as $\Delta\rho_i(\boldsymbol{r}) = \Delta n(\boldsymbol{r} - \boldsymbol{r}_i) - \delta(\boldsymbol{r} - \boldsymbol{r}_i)$. Integrating the δ-function parts and regarding the two atoms as equivalent, eqn. (3) can be written as

$$\Delta E_{es}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} - 2\int \mathrm{d}\boldsymbol{r} \frac{2\Delta n(\boldsymbol{r} - \boldsymbol{r}_1)}{|\boldsymbol{r} - \boldsymbol{r}_2|} + \int\int \mathrm{d}\boldsymbol{r}\ \mathrm{d}\boldsymbol{r}' \frac{2\Delta n(\boldsymbol{r} - \boldsymbol{r}_1)\Delta n(\boldsymbol{r}' - \boldsymbol{r}_2)}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{4}$$

The second and third terms can be expressed using an induced potential v_s in eqn. (2) as

$$\Delta E_{es}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} - 2v_s(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) + \int \mathrm{d}\boldsymbol{r}\ \Delta n(\boldsymbol{r} - \boldsymbol{r}_1)v_s(\boldsymbol{r} - \boldsymbol{r}_2) \tag{5}$$

The change in exchange-correlation energy is written as

$$\Delta E_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \int \mathrm{d}\boldsymbol{r}\Big[f_{xc}(n_0 + \Delta n_1 + \Delta n_2) - \sum_{i=1}^{2} \Big\{ f_{xc}(n_0 + \Delta n_i) - f_{xc}(n_0) \Big\} - f_{xc}(n_0) \Big] \tag{6}$$

where Δn_i is the electron density induced by atom i and f_{xc} is expressed as $f_{xc}(n) = e_{xc}(n)n$ with e_{xc} the exchange-correlation energy density. The expansion of f_{xc} into the linear term of induced density reduces the expression of ΔE_{xc} to

$$\Delta E_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2) = 2\int \mathrm{d}\boldsymbol{r}\phi_{xc}(\boldsymbol{r} - \boldsymbol{r}_1)\Delta n(\boldsymbol{r} - \boldsymbol{r}_2) \tag{7}$$

where ϕ_{xc} is defined as $\phi_{xc}(n(\boldsymbol{r})) = v_{xc}\{n_0 + \Delta n(\boldsymbol{r})\} - v_{xc}(n_0)$ and v_{xc} is defined as $v_{xc} = \mathrm{d}f_{xc}/\mathrm{d}n$. Since the kinetic energy of inhomogeneous electron gas is expressed as

$$\frac{3}{5}(3\pi^2)^{2/3}\int \mathrm{d}\boldsymbol{r}(n(\boldsymbol{r}))^{5/3}$$

the change in kinetic energy is obtained using the same procedure with eqn. (6), and is written as [8]

$$\Delta E_{kin}(\boldsymbol{r}_1, \boldsymbol{r}_2) = 2\int \mathrm{d}\boldsymbol{r}k(\boldsymbol{r} - \boldsymbol{r}_1)\Delta n(\boldsymbol{r} - \boldsymbol{r}_2) \tag{8}$$

where function k is defined as

$$k(\boldsymbol{r} - \boldsymbol{r}_1) = (3\pi^2)^{2/3}[\{n_0 + \Delta n(\boldsymbol{r} - \boldsymbol{r}_1)\}^{2/3} - n_0^{2/3}]$$

Adding ΔE_{es}, ΔE_{xc} and ΔE_{kin}, the pair potential between two deuterium atoms is obtained as a function of separation r and is written as

$$V_{D-D}(r) = \frac{2}{r} - 2v_s(r) + \int dr' \, \Delta n(r')\{v_s(|r - r'|) + 2\phi_{xc}(|r - r'|) + 2k(|r - r'|)\} \tag{9}$$

The first term describes direct coulomb interaction, the second describes interaction between one nucleus and electrons belonging to another nucleus, and the third describes interaction between electrons belonging to one nucleus and another nucleus. The third term is reduced by choosing the argument as $x = |r - r'|$, and then $V_{D-D}(r)$ is rewritten as

$$V_{D-D}(r) = \frac{2}{r} - 2v_s(r) + \frac{2\pi}{r} \int dr' r' \, \Delta n(r') \int_{|r-r'|}^{r+r'} dx x\{v_s(x) + 2\phi_{xc}(x) + 2k(x)\} \tag{10}$$

The starting points of our D–D pair potential in eqns. (3) and (5) are similar to those of Nørskov [9], which are derived for H_2 in copper and nickel using effective medium theory based on the density functional formalism.

The results of the calculation of V_{D-D} in eqn. (10) are plotted in Fig. 4. From Fig. 4, it is seen that three terms are cancelled at large values of r, and the second term causes the potential well. This well is very shallow and its bottom is broad and flat.

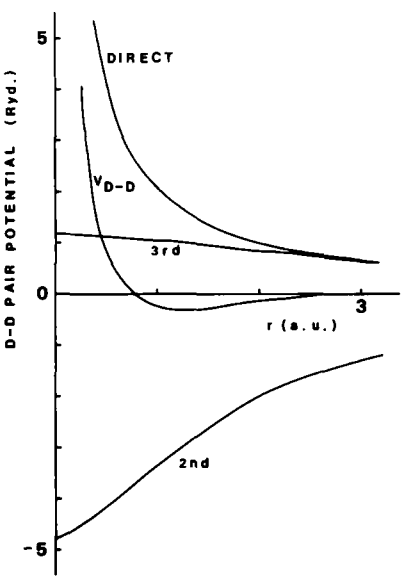

Fig. 4. D–D pair potential: the direct, 2nd and 3rd terms are the contributions from each term of eqn. (4).

3. D–Pd pair potential

Pettifor [6, 7] constructed the pseudopotential for 4d-transition metals assuming that d electrons move rigidly with the ion and conduction electrons respond to an effective bare pseudopotential. Therefore, the screened pseudopotential is written as

$$V_{\mathrm{scr}}(r) = \frac{1}{2}\exp(-q_{\mathrm{TF}}r)V_{\mathrm{RMT}}(r) \quad \text{for} \quad r < r_{\mathrm{c}} \tag{11}$$

where q_{TF}, r_{c} and $V_{\mathrm{RMT}}(r)$ are the Thomas–Fermi screening constant, empty core parameter and rigid muffin-tin potential respectively. The D–Pd pair potential is written as

$$V_{\mathrm{D-Pd}}(r) = V_{\mathrm{dir}}(r) + \int \mathrm{d}\boldsymbol{r}'\, \Delta n(r')V_{\mathrm{scr}}(|\boldsymbol{r} - \boldsymbol{r}'|) \tag{12}$$

where $r_{\mathrm{c}} = 1.79$ u [6, 7]. In eqn. (12), the second term describes the interaction between the palladium atom and the induced electron screen around the deuterium atom, the first term describes the direct interaction between palladium and deuterium which is written as

$$V_{\mathrm{dir}}(r) = \frac{2Z}{r}\exp(-q_{\mathrm{TF}}r) - \frac{C}{r}\exp(-q_{\mathrm{TF}}r)\{q_{\mathrm{TF}}r\cosh(q_{\mathrm{TF}}r) - \sinh(q_{\mathrm{TF}}r)\} \quad \text{for} \quad r < r_{\mathrm{c}}$$

and

$$V_{\mathrm{dir}}(r) = \frac{2Z}{r}\exp(-q_{\mathrm{TF}}r) - \frac{C}{r}\exp(-q_{\mathrm{TF}}r)\{q_{\mathrm{TF}}r_{\mathrm{c}}\cosh(q_{\mathrm{TF}}r_{\mathrm{c}}) - \sinh(q_{\mathrm{TF}}r_{\mathrm{c}})\} \quad \text{for} \quad r > r_{\mathrm{c}} \tag{13}$$

In eqn. (13), the first term is the interaction between nuclei of a deuterium and a palladium atom with $Z = 10$, the second term is the interaction between deuterium and the 4d electrons around the palladium atom and the factor C is selected as $\lim_{r\to\infty} V_{\mathrm{dir}}(r) = 2N_{\mathrm{s}}\exp(-q_{\mathrm{TF}}r)/r$. Choosing the same argument as for eqn. (10), eqn. (12) is reduced to

$$V_{\mathrm{D-Pd}}(r) = V_{\mathrm{dir}}(r) + \frac{1}{r}\exp(q_{\mathrm{TF}}r_{\mathrm{c}})\int \mathrm{d}r'r'\,\Delta n(r')\int_{|r-r'|}^{r+r'} \mathrm{d}x x\exp(-q_{\mathrm{TF}}x)V_{\mathrm{RMT}}(x)\theta(x - r_{\mathrm{c}}) \tag{14}$$

where θ is the usual step function and V_{RMT} is written as

$$V_{\mathrm{RMT}}(r) = \begin{cases} -\dfrac{2Z}{r} & \text{for } r < R_{\mathrm{WS}} \\ V_{\mathrm{RMT}}(R_{\mathrm{WS}}) & \text{for } r > R_{\mathrm{WS}} \end{cases} \tag{15}$$

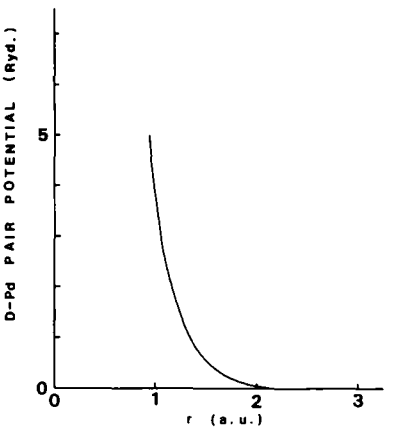

Fig. 5. D–Pd pair potential.

where R_{WS} is the Wigner–Seitz radius of the host ion. We used eqn. (14) to obtain the D–Pd pair potential plotted in Fig. 5. A value of $q_{TF} = 0.895$ a.u. was used in making calculations and was obtained as follows:

$$q_{TF} = (4k_F/\pi)^{1/2} \quad k_F = (3\pi^2 n_0)^{1/3} \quad n_0 = (4\pi r_s^3/3)^{-1}$$

$$r_s = 3.05 \text{ u}$$
$$n_0 = 8.41 \times 10^{-3} \text{ u}$$
$$k_F = 6.29 \times 10^{-1} \text{ u}$$

4. The solution of the Schrödinger equation for deuterium in the potential energy field

As outlined in Section 1, we consider the f.c.c. palladium lattice to include a deuterium atom at the nearest neighbor O site from a vacancy to estimate the distance between an included deuterium atom at an O site and an embedded deuterium atom. The potential energy field experienced in this lattice by an embedded deuterium atom is described as

$$\Phi(\boldsymbol{r}) = V_{D-D}(|\boldsymbol{r} - \boldsymbol{r}_{oc}|) + \sum_n {}' V_{D-Pd}(|\boldsymbol{r} - \boldsymbol{r}_n|) \tag{16}$$

where $\boldsymbol{r}_{oc}$ and $\boldsymbol{r}_n$ are the positions of an O site and the nth lattice point respectively. In eqn. (16), the prime of the second term denotes that the vacancy site is omitted from the lattice summation. Rapid convergence in this lattice summation is seen within the 8th neighbor lattice point from the vacancy, because of the screening factor $\exp(-q_{TF}r)$ of V_{D-Pd} in eqn. (14). The results are plotted in Fig. 6 along the x axis and in Fig. 7 for the x–y plane. Looking at Figs. 6 and 7, there is a shallow well of potential caused by a minimum in V_{D-D} as described in Section 3. If the deuterium atom could be trapped in the well, it would be very curious, because the distance between

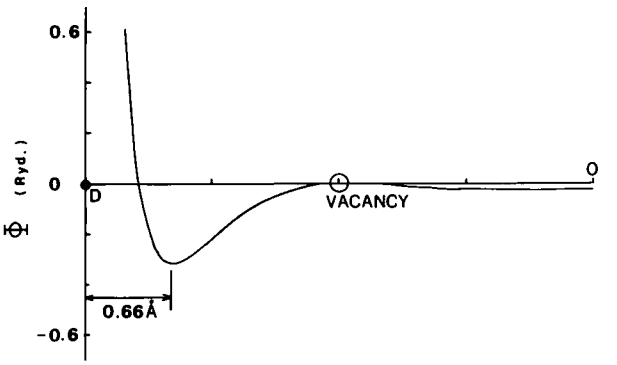

Fig. 6. Potential energy field experienced by the embedded deuterium atom. The plot is along the x axis.

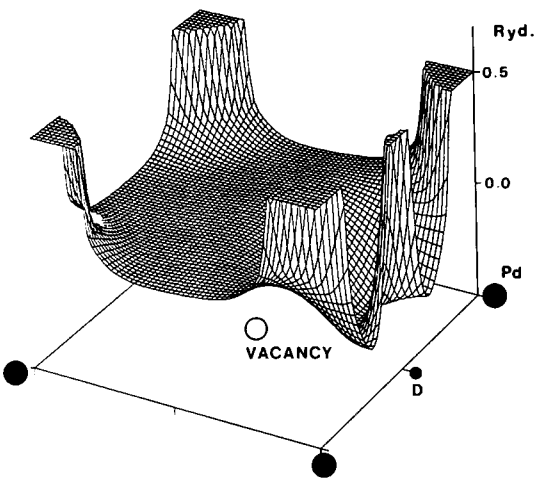

Fig. 7. Potential energy field experienced by the embedded deuterium atom. The plot is for the $x-y$ plane.

the deuterium atom at the O site and the trapped deuterium atom is about 0.66 Å, which is smaller than the usual distance between nuclei of the D_2 molecule (0.74 Å). The behavior of the deuterium atom as a quantum particle is described by the Schrödinger equation which is written as

$$\left\{-\frac{1}{M}\nabla^2 + \Phi(\boldsymbol{r})\right\}\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{17}$$

where M is the mass ratio of a deuterium atom to an electron.

The full three-dimensional calculations of eqn. (17) were done using a numerical relaxation technique first presented by Kinball and Shortley [10] and used by Puska and Nieminen [11] outlined as follows. For the ground

state, a numerical solution is obtained by iterative use of the next two equations:

$$\psi_{ijk}{}^{n+1} = \frac{f_{ijk}}{6 + Md^2(\Phi_{ijk} - E^n)} \tag{18}$$

and

$$E^n = -\frac{1}{Md^2} \frac{\sum_{ijk} \psi_{ijk}{}^n \{f_{ijk} - (6 + Md^2\phi_{ijk})\psi_{ijk}{}^n\}}{\sum_{ijk} (\psi_{ijk}{}^n)^2} \tag{19}$$

where the subscripts enumerate the mesh point, the superscripts give the order of iteration, d is the spacing of the mesh, and f_{ijk} is defined as $f_{ijk} = \psi_{i+1,j,k}{}^n + \psi_{i-1,j,k}{}^n + \psi_{i,j+1,k}{}^n + \psi_{i,j-1,k}{}^n + \psi_{i,j,k+1}{}^n + \psi_{i,j,k-1}{}^n$

From this process, we obtained the trapped solution of energy eigenvalue $E = 0.011$ Ryd, where the origin of the energy is the bottom of the potential. The shape of the wave function plotted in Fig. 8 for the x–y plane has a sharp peak at the potential well. Therefore, the distance between included deuterium atom at the O site and the trapped deuterium atom is estimated to be 0.66 Å.

5. Conclusions

The electronic screening cloud around a deuterium atom in palladium decreases the repulsive interaction and produces a minimum in V_{D-D}. This minimum causes the shallow well of the potential experienced by embedded deuterium atoms in a palladium lattice, which contains a deuterium atom at a nearest neighbor O site from a vacancy. The trapped solution to the potential well is obtained and the nearest neighbor D–D distance is estimated to be 0.66 Å, which is smaller than the molecular value 0.74 Å.

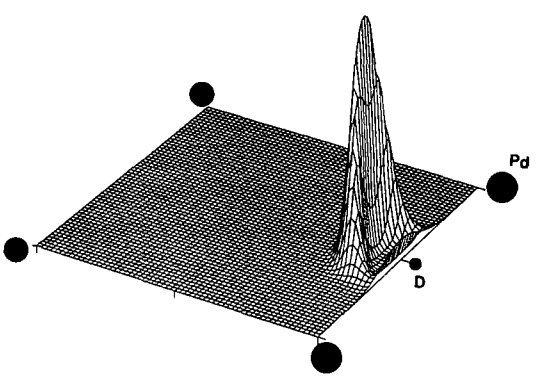

Fig. 8. Wave function of a trapped deuterium atom in the potential well.

Similar calculations were carried out by other groups. The results of Sun and Tomanek [12] for H–H distance, which is estimated from the cohesive energy of PdH_2 as a function of H–H separation, is 0.94 Å. The results of Wang *et al.* [13] for the H–H distance, which is calculated using a first-principles pseudopotential total-energy approach along the [100] orientation, is 1.06 Å (2.0 a.u.). Wei and Zunger [14] also studied the stability of diatomic hydrogen in f.c.c. palladium. Their result for H–H separation along the [001] direction is 0.95 Å. The difference between our result and their results may depend on the expression for the H–H interaction. In this paper, we considered the f.c.c. palladium lattice containing a vacancy and estimated the D–D separation, while the above mentioned groups [12–14] considered a perfect lattice. This may cause the difference between our result and their results for the D–D separation. However, our calculation did not include the effects of lattice relaxation around a vacancy, so a more sophisticated treatment may show the significance of this point.

References

1 M. Fleishman, S. Pons and M.J. Hawkins, *J. Electroanal. Chem.*, *261* (1989) 301.
2 S. E. Jones, E. P. Palmer, J. B. Czirr, D. L. Decker, G. L. Jensen, J. M. Thorne, S. F. Taylor and J. Rafelski, *Nature (London)*, *338* (1989) 737.
3 W. Kohn and L. J. Sham, *Phys. Rev. A*, *140* (1965) 113.
4 M. Mannienen, R. Nieminen, P. Hautojarvi and J. Arponen, *Phys. Rev. B*, *12* (1975) 4012.
5 K. Tsuchiya, M. K. Kunio, K. Ohashi, Y. H. Ohashi and M. Fukuchi, *J. Phys. Soc. Jpn. 54* (1985) 2588.
6 D. G. Pettifor, *J. Phys. F*, *7* (1977) 613.
7 D. G. Pettifor, *J. Phys. F*, *7* (1977) 1009.
8 W. A. Harrison, *Electronic Structure and the Properties of Solids*, W. H. Freeman, 1980.
9 J. K. Nørskov, *Phys. Rev. B*, *20* (1979) 446.
J. K. Nørskov, *Phys. Rev. B*, *35* (1987) 7423.
J. K. Nørskov, *J. Chem. Phys.*, *90* (1989) 7461.
10 G. E. Kimball and G. H. Shortley, *Phys. Rev.*, *45* (1934) 815.
11 M. J. Puska and R. M. Nieminen, *Phys. Rev. B*, *29* (1984) 5382.
12 Z. Sun and D. Tomanek, *Phys. Rev. Lett.*, *63* (1989) 53.
13 X. W. Wang, S. G. Louie and M. L. Choen, *Phys. Rev. B*, *40* (1989) 5822.
14 S. Wei and A. Zunger, *Solid State Commun.*, *73* (1990) 327.