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# Theory of light interstitials in bcc metals. I. Self-trapped state of hydrogen and muons in Nb

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A quantum-mechanical calculation has been performed on the self-trapped state of hydrogen isotopes and positive muons in Nb. By solving a Schrödinger equation for these light interstitials in the field of interaction with surrounding metal atoms, the energy and the wave function of the interstitials and the displacements of metal atoms have been derived. It is concluded, in particular, that hydrogen isotopes occupy tetrahedral (*T*) sites, and positive muons occupy octahedral (*O*) sites in Nb. The origin of the systematic variation of the relative stability of *O* sites vs *T* sites is clarified. Some calculations performed on the excited state are also described.

## I. INTRODUCTION

A theoretical possibility that hydrogen atoms in metals are in band states in which wave functions are extended over periodic arrays of interstitial sites appears to be largely disproved by observations. Even in bcc metals, where extended states are more likely to form than in fcc metals due to smaller separation between interstitial sites, experimental results show clearly that H atoms are localized in space.

As evidence for the localization, three kinds of observations on hydrogen in group-V metals (V, Nb, and Ta) may be cited.

(1) Channeling experiments[1]: The occupancy of tetrahedral (*T*) sites has been established for H and D in the $\alpha$ phase.

(2) The inelastic scattering of neutrons[2]: For H in the $\alpha$ phase, peaks have been found at 0.17 and 0.12 eV with the intensity ratio of 2:1. For D in the $\alpha$ phase, the energy values are reduced approximately by a factor of 1.4. These results have been interpreted by regarding a H(D) atom as three harmonic oscillators localized around a *T* site.

(3) The force-dipole tensor P (Ref. 3): Two different types have been found as regards the anisotropy of the force-dipole tensor that represents the average stress field around a H(D) atom. One is the type characterized by a small anisotropy, observed in many cases including $\alpha$-$VH_x$, $\alpha$- and $\delta$-$VD_x$, and all phases of hydrides and deuterides of Nb and Ta. The other is the type characterized by a large anisotropy, observed in $\beta$- and $\delta$-$VH_x$ and $\beta$-$VD_x$. The former is identified as the *T*-site occupancy, and the latter as the *O*-site occupancy. In the latter, the magnitude of the anisotropy is found to be nearly the same as heavier interstitials (C, N, O) known to occupy *O* sites in bcc metals.[4]

A possibility for simultaneous occupation of a group of interstitial sites have also been considered. Birnbaum and Flynn[5] once proposed that a H(D) atom in Nb is in a "pocket state," which is a tunneling state extending over a group of four *T* sites (4*T* in Sec. II). The proposal was made to account for reported anomalies in the Debye-Waller factor and the specific heat at low temperatures. However, it proved later that the former was due to inappropriate analysis of data[6] and the latter was due to the presence of other interstitial impurities (O and/or N) in addition to H.[7] Thus we no longer have any experimental observation that requires the existence of tunneling states.

On theoretical grounds, the localization must be a consequence of strong interactions between H(D) and metal (*M*) atoms. The strong interaction can lead to a formation of the "self-trapped state," in which the total energy is lowered by confining a H(D) atom in the potential well produced by a local relaxation of the metal lattice. A calculation of the self-trapping effect has been performed by Kehr,[8,9] who adopted a harmonic approximation for the interaction potential, and estimated the strength of the H-*M* interaction from the observed P-tensor values, and the *M*-*M* interaction with recourse to isotropic elasticity theory. Hence, the self-trapping energy of about 0.20 eV has been obtained for H in Nb.[8,9] Although his calculation is inadequate in that he regarded H atoms as classical particles, the energy value obtained suggests strongly that the self-trapping distortion should take place and make H(D) atoms more or less localized in space.

In the present paper, we intend to make a step towards better understanding the nature of the self-trapped state by performing quantum-mechanical calculations on the light interstitials in Nb. We solve a Schrödinger equation for a H atom in the field of interaction with surrounding metal atoms, and try to find a configuration of *M* atoms that minimizes the total energy, including the energy of a H atom and the energy of distortion of the surrounding metal lattice. Our calculation differs from Kehr's treatment[8,9] in the following two respects: First, the light interstitial is regarded as a quantum-mechanical entity, the state of which is described by a Schrödinger equation. The energy of a H atom thus includes both kinetic and potential energies. Second, the interaction between the light interstitial and $M$ atoms is written as a sum of double Born-Mayer potentials. For the interaction between $M$ atoms, the lattice Green's function,[10] based on the harmonic approximation, is adopted. In the frame of the adiabatic approximation, the interaction potential between H and $M$ atoms should, in principle, be obtained from the calculation of the electronic energy as a function of configuration of $M$ atoms. In practice, however, no such potentials being available, we are forced to construct a potential on empirical grounds, and furthermore, reduce it into a sum of two-body, central potentials in order to make the computation tractable. Therefore, we choose potential parameters that reproduce experimental values of the excitation energy and the force-dipole tensor simultaneously, and examine if a consistent understanding of many other properties can be attained on this basis. It must be admitted here that the reliability of the calculation is limited by the use of this approximate potential, but it may still be expected that the calculation will help to reveal some general aspects of the quantum-mechanical nature of the problem.

The quantum-mechanical description of the state, in terms of energy eigenvalues and wave functions, is also expected to be necessary in investigating the migration process of light interstitials in bcc metals. In fact, Kehr[8,9] has obtained crude estimates of the tunneling matrix element based on model wave functions, and found that their magnitude is large enough to play an important role in the migration of H(D) atoms in group-V metals. Since the tunneling process depends critically on the wave function, more realistic quantum-mechanical calculations are obviously needed.

Some calculations are also performed on positive muons in Nb. A positive muon can be treated in the same formalism by substituting $\frac{1}{9}$ of the proton mass into the Schrödinger equation. Although many people simply assume that positive muons occupy the same type of sites as hydrogen isotopes, this appears to be rather questionable in bcc metals. Since potential minima for interstitials are expected to be rather shallow in bcc as compared to fcc metals, the behavior of muons in these two structures can be very different. Therefore, no analogy should be made with the case of Cu, where experiments[11] as well as quantum-mechanical calculations[12] have established that muons, like hydrogen isotopes, occupy $O$ sites. Since experiments do not allow unambiguous determination of the site of muons in bcc metals, the application of the present calculation to this problem is believed to be of value.

In Sec. II, a general formulation for the calculation of self-trapped states is described. A method for constructing an empirical interaction potential is described in Sec. III, followed by presentation of numerical results in Sec. IV. Results are discussed in Sec. V, regarding the relative stability of $T$ and $O$ sites, the state of positive muons, and the nature of the excited state.

## II. FORMULATION

Let us consider a system which consists of a light interstitial atom and $N$ host metal ($M$) atoms. If the interstitial atom follows the motion of $M$ atoms adiabatically, the energy of the whole system can be written as

$$E(\{u_i^m\},\alpha)=E_L(\{u_i^m\})+E_\alpha(\{u_i^m\}) \ , \tag{1}$$

where $\{u_i^m\}$ is a set of displacements of $M$ atoms, $E_L$ is the energy of interaction between $M$ atoms in the presence of the interstitial atom, and $E_\alpha$ is one of the energy eigenvalues of a Schrödinger equation

$$[-(\hbar^2/2\mathfrak{M})\nabla^2+U]\psi_\alpha=E_\alpha\psi_\alpha \tag{2}$$

for the interstitial atom of mass $\mathfrak{M}$. In the harmonic approximation, $E_L$ is given in terms of the dynamic matrix element as

$$E_L=\tfrac{1}{2}u_i^m\phi_{ij}^{mn}u_j^n \ . \tag{3}$$

A convention of repeated indices is used. As regards the potential $U$ in the Schrödinger equation, we assume that it may be written as a sum of two-body interaction potentials with surrounding $M$ atoms;

$$U=\sum V(|\vec{R}^m+\vec{u}^m-\vec{r}|) \ , \tag{4}$$

where $\vec{R}^m$ is the position of the $m$th atom in the unloaded lattice. Note that the energy eigenvalue and the wave function depend on displacements of M atoms.

The equilibrium configuration is such that the adiabatic potential, Eq. (1), takes the lowest value as a function of displacements of $M$ atoms. This defines the self-trapped state. The displacement can be obtained from the condition

$$\partial E/\partial u_i^m=0 \tag{5}$$

or equivalently

$$u_i^m=G_{ij}^{mn}F_j^n \ , \tag{6}$$

by using the lattice Green's function $G_{ij}^{mn}$. The lattice Green's function is defined by $G_{ij}^{mn}\phi_{jk}^{nl} = \delta_{ml}\delta_{ik}$. $F_j^n$ is a force exerted by the interstitial atom on the $n$th $M$ atom in the direction $j$, and is given by

$$F_j^n = -\int d\vec{r}\,|\psi_\alpha|^2\,\partial V(|\vec{R}^n + \vec{u}^n - \vec{r}|)/\partial u_j^n. \qquad (7)$$

A procedure adopted for numerical solution is as follows:

(1) We start by assuming appropriate values for the displacements of $M$ atoms, and calculate the potential energy $U$ for this configuration.

(2) Using this potential, we solve the Schrödinger equation [Eq. (2)] numerically and obtain the energy eigenvalue $E_\alpha$ and the wave function $\psi_\alpha$ of the interstitial by using the method of Kimball and Shortley.[13]

(3) We calculate the forces $F_j^n$ acting on $M$ atoms from Eq. (7) and concomittant displacements of $M$ atoms from Eq. (6).

(4) The whole procedure is to be repeated until self-consistency is attained as regards displacements of $M$ atoms.

It must be recognized that Eq. (6) is satisfied by all possible configurations in which $E$ takes extremal values (both minimum and maximum) as a function of displacements; it does not necessarily lead to the lowest value of the energy. Therefore, we have examined three possible configurations in order to find the configuration of the lowest energy. The three configurations, labeled as $1T$, $4T$, and $6T$ are shown in Fig. 1. Other possible configurations, such as $2T$, will be examined in a forthcoming paper in connection with migration processes. For each configuration, displacements of the first- and second-nearest-neighbor $M$ atoms are calculated by the approximation that the direct force from the interstitial atom, given by Eq. (7), acts only on these $M$ atoms. The Schrödinger equation is solved under the condition that the wave function be zero on the boundary of some specified region around the interstitial atom. The interval between mesh points on which the equation is evaluated is $0.025a \sim 0.035n$. A more detailed explanation for each configuration is given below.

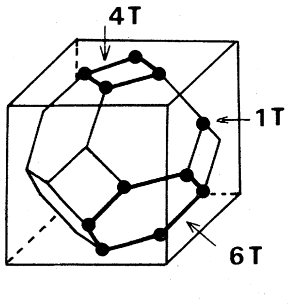

FIG. 1. Three possible configurations ($1T$, $4T$, and $6T$) for light interstitials in bcc metals.

### 1. 1T state

When one of the tetrahedral sites is taken as the origin and the Cartesian axes parallel to the crystallographic axes, coordinates of four nearest-neighbor $M$ atoms of the $T$ site are of the type $(a/2, 0, -a/4)$ and four second nearest neighbors are of the type $(a/2, 0, 3a/4)$. The displacement and the force for the atom at $(a/2, 0, -a/4)$ are written as $(u_1, 0, -u_2)$ and $(F_1, 0, -F_2)$, respectively; corresponding quantities for the atom at $(a/2, 0, 3a/4)$ are written as $(u_3, 0, u_4)$ and $(F_3, 0, F_4)$, respectively.

The region in which the wave function is nonzero is taken to be a cube of length $a$ having the $T$ site at the center. In actual calculations, the volume can be reduced to one-fourth of this region by symmetry considerations.

### 2. 4T state

In this configuration, a group of four $T$ sites having an $O$ site at the center (Fig. 1) is treated as a unit, assuming that the symmetry around the $O$ site is conserved. Coordinates of the two nearest neighbors and four second-nearest neighbors of the $O$ site are given by $(\pm a/2, 0, 0)$ and $(0, \pm a/2, \pm a/2)$, respectively. The displacement and the force for the atom at $(a/2, 0, 0)$ are written as $(u_1, 0, 0)$ and $(F_1, 0, 0)$, respectively; corresponding quantities for the atom at $(0, a/2, a/2)$ are written as $(0, u_3, u_3)$ and $(0, F_3, F_3)$, respectively.

The region in which the wave function is nonzero is taken to be an octahedron formed by the first- and second-nearest-neighbor $M$ atoms of the $O$ site. The volume can be reduced to one-eighth by symmetry.

Note that the symmetry of this configuration allows for the $O$-site occupation as a particular case. In fact, there is a continuous change from $4T$ to $O$ state depending on the strength of the interaction (Sec. IV).

### 3. 6T state

In this configuration, a group of six $T$ sites forming a regular hexagon (Fig. 1) is treated as a unit, assuming that the symmetry around the center of these $T$ sites is conserved. Coordinates of two nearest neighbors of the center point are given by $(\pm a/4, \pm a/4, \pm a/4)$ and those of six second-nearest neighbors are of the type $(-a/4, -a/4, +3a/4)$. The displacement and the force for the atom at $(a/4, a/4, a/4)$ are written as $(u_1, u_1, u_1)$ and $(F_1, F_1, F_1)$, respectively, and corresponding quantities for the atom at $(-a/4, -a/4, 3a/4)$ are written as $(-u_3, -u_3, u_4)$ and $(-F_3, -F_3, F_4)$, respectively.

The region in which the wave function is nonzero is taken to be a polyhedron formed by the first- and second-nearest-neighbor $M$ atoms of the center point. The volume can be reduced to one-sixth by symmetry.

In the calculation of the energy separation to be determined from the inelastic scattering of neutron, we start by calculating the ground-state configuration as described above, and then solve the Schrödinger equation for the excited state by keeping the position of surrounding $M$ atoms in their ground-state configuration. The procedure is based on the assumption that the transition occurs adiabatically. For the calculation of the excited state, we solve the Schrödinger equation by imposing a boundary condition which automatically makes the wave function orthogonal to the ground-state function. In the case of $1T$ configuration, for example, the doubly degenerate excited state can be derived by imposing a boundary condition that the wave function be zero on a plane passing through the $T$ site at $(0,0,0)$ and a pair of nearest-neighbor $M$ atoms at $(0, \pm a/2, a/4)$.

## III. INTERACTION POTENTIAL

In contrast to the case of impurity atoms in nearly free electron metals where the total energy can be written as a sum of pseudopotentials and a volume-dependent energy of free electrons, there is no theoretically justifiable and yet computationally feasible description of the energy for hydrogen in transition metals. Some simplification is therefore unavoidable. As for the volume-dependent but structure-independent energy of electrons contributed by H atoms to the conduction band of a host metal, there is an empirical justification for neglecting it: Experiments have shown that both the local lattice distortion and the average lattice dilatation produced by H atoms can be consistently described in terms of a P tensor,[3] and accordingly that H atoms can be simply regarded as force centers in the elastic medium. The decomposition of the structure-dependent energy into a sum of two-body, central potentials [Eq. (4)] is admittedly more questionable, but is supported to some extent by the formation of bonding states observed by the x-ray and electron spectroscopy,[14] and the expectation that these states may be regarded to form primarily between a pair of H and $M$ atoms.[15]

In the following, we construct a potential between a proton and a Nb atom. The first source of information we use for determining the interaction potential is the force-dipole tensor P. For an interstitial atom on a site of axial symmetry, the tensor P takes the form

$$\mathsf{P} = \begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & B \end{pmatrix} . \tag{8}$$

In microscopic terms, the components of P are given by[16]

$$P_{ij} = F_i^m R_j^m . \tag{9}$$

Experimental values of the diagonal sum and the anisotropy of the P tensor for H atoms in group-V metals are compiled in Table I. The fact that TrP is positive means that the interaction is repulsive at ordinary distances between H and $M$ atoms. As for the anisotropy, very small values of $|A - B|$ signifies that a long-range stress field around a H atom on a $T$ site is very nearly isotropic.

Bauer *et al.*[24,29] have interpreted this isotropic stress field as a result of appropriate balance of forces acting on the first- and second-nearest-neighbor $M$ atoms. For a perfect isotropy, it is required from Eq. (9) that the magnitude of these forces, $f_1$ and $f_2$, respectively, should be in the ratio $f_1/f_2 = 4.34$. If we regard a H(D) atom as a classical particle, and adopt a Born-Mayer form $V_0 e^{-r/\rho}$ for the potential from which the force is to be derived by differentiation, the parameter $\rho$ should be equal to $a/4.3$ in order to reproduce the ratio $f_1/f_2$. We have reached nearly the same result ($\rho \simeq a/4.6$) from the quantum-mechanical calculation described in this paper, assuming a Born-Mayer form for the interaction potential. In this case, the force is to be calculated from Eq. (7).

The second source of information that we make use of is the excitation energy of protons determined from the inelastic scattering of neutrons. In the case of protons in the $\alpha$ hydrides of group-$V$ metals, the excitation energies, $\Delta E_1 = 0.17$ eV and $\Delta E_2 = 0.12$ eV, have been found to be largely independent of host metals. The intensity ratio of these transitions (2 : 1) is consistent with the local symmetry of a $T$ site. When a proton is regarded as harmonic oscillators, the curvature of the harmonic potential deduced from these energy values turns out to be such that it requires a steeply varying, short-range interaction potential between a pair of H and $M$ atoms. We have found from quantum-mechanical calculations assuming a Born-Mayer form for the interaction potential that $\rho$ should be $a/18$ in order to reproduce $\Delta E_1$ and TrP. The fact that a Born-Mayer potential cannot reproduce simultaneously the isotropic stress field and the excitation energy does not seem to be well recognized.

We note here that this apparent contradiction

TABLE I. Reported values of the force-dipole tensor for H(D) atoms in group-V metals.

| Metal | Isotope | Phase | TrP (eV) (=$A+2B$) | $\frac{3\lvert A-B\rvert}{\mathrm{TrP}}$ | Method | Reference |
|---|---|---|---|---|---|---|
| V | H, D | ($\beta$) | 6.85 | 0.978 | $\frac{\Delta a}{a}, \frac{\Delta c}{c}$ | Westlake (Ref. 17)[a] |
| | | | | | | Asano *et al.* (Ref. 18)[a] |
| | H | ($\alpha$) | 7.55 | | $\Delta a/a$ | Maeland (Ref. 20)[b] |
| | D | ($\alpha$) | 6.68 | | $\Delta a/a$ | Hardcastle *et al.* (Ref. 21)[c] |
| | H, D | ($\alpha$) | 7.71 | | $\Delta L/L$ | Magerl *et al.* (Ref. 22) |
| Nb | H | ($\beta$) | 8.371 | 0.046 | Crystal structure | Pick *et al.* (Ref. 23)[d] |
| | | | 8.563 | 0.011 | | |
| | D | ($\alpha$) | 8.5±1.0 | 0.08 | Neutron scatt. | Bauer *et al.* (Ref. 24) |
| | H, D | ($\alpha$) | 9.63 | | $\Delta L/L$ | Magerl *et al.* (Ref. 22) |
| | H, D | ($\alpha$) | 9.99 | | $\Delta a/a$ | Pfeiffer *et al.* (Ref. 25)[c] |
| | H | ($\alpha$) | 10.1±0.3 | ≤0.06 | x-ray scatt. | Metzger *et al.* (Ref. 26) |
| Ta | H | ($\alpha$) | | ≤0.08 | Snoek effect | Buchholz *et al.* (Ref. 27) |
| | H, D | ($\alpha$) | 9.95 | | $\Delta L/L$ | Magerl *et al.* (Ref. 22) |
| | H | ($\alpha$) | 10.32 | | $\Delta a/a$ | Pfeiffer *et al.* (Ref. 25)[c] |
| | D | ($\alpha$) | 9.51 | | | |
| | H | ($\alpha$) | 10.1±0.5 | ≤0.06 | x-ray scatt. | Metzger *et al.* (Ref. 28) |

[a] Evaluated from extrapolation of the literature values of $\Delta a/a$ and $\Delta c/c$ to 0 K, and the elastic constants at 4.2 K reported by Bolef *et al.* (Ref. 19).

[b] Evaluated from the literature value of $\Delta a/a$ at 200 °C, and the elastic constants extrapolated from the data of Ref. 19.

[c] Evaluated from the literature value of $\Delta a/a$ and the elastic constants reported in Ref. 22, both at room temperature.

[d] Evaluated at 160 °C.

regarding the range of the interaction potential can be reconciled by recognizing that the excitation energy is essentially determined by the potential at short distances from the H atom, whereas the force-dipole tensor is more sensitive to the potential at larger distances. What the apparent contradiction really means is that the interaction potential must be steeply varying at short distances, with a long-range tail superposed on it. As a potential of this form, we adopt a sum of two exponential functions, which we call a double Born-Mayer potential; i.e.,

$$V(r)=V_1e^{-(r-\sqrt{5}a/4)/\rho_1}+V_2e^{-(r-\sqrt{5}a/4)/\rho_2}\,, \tag{10}$$

with $\rho_1<\rho_2$. The four parameters in the potential are determined by fitting to experimental values in the following way: We first determine the first term (a short-range part) by fitting to $\Delta E_1$ and TrP, the second term (a long-range part) by fitting to TrP and the isotropy condition $A=B$, and finally making a small adjustment. Values adopted for H in Nb are

$$V_1=0.1\text{ eV},\quad V_2=0.6\text{ eV},\quad \rho_1=a/40,\quad\text{and}\quad \rho_2=a/3\,, \tag{11}$$

with $a=3.3$ Å. Calculated values of the excitation energy and the force-dipole tensor for the $1T$ configuration by use of these potential parameters are $\Delta E_1=0.165$ eV and TrP $=10.35$ eV, $A-B=0.42$ eV, respectively. The agreement with experimental values listed in Table I is believed to be good enough for our purpose, and no further effort for a better fitting has been made.

Numerical results may depend to some extent on the choice of the Green's function. In the present calculation, the Green's function given by Tewary[30] has been adopted.

## IV. NUMERICAL RESULTS

### A. Hydrogen isotopes (H,D,T) in Nb

Results of the calculation on the self-trapped state of hydrogen isotopes (H, D, T) are given in Table II for three different configurations ($1T, 4T, 6T$). It concludes a change of the ground-state energy caused by the self-trapping distortion of the lattice ($\Delta E_0$), the energy of distortion of the surrounding lattice ($E_L$), the self-trapping energy ($\Delta E=\Delta E_0+E_L$), components of the displacement of first- and second-neighbor $M$ atoms ($u_1\sim u_4$), the magnitude and the anisotropy of the stress field [TrP and $3(A-B)/$TrP, respectively].

One of the most important results is that the $1T$ configuration has lower self-trapping energies than $4T$ and $6T$ configurations, and is therefore the most stable one for all isotopes H, D, and T. We shall hereafter disregard $6T$ configuration because it has much higher self-trapping energies

TABLE II. Properties of the self-trapped state of hydrogen isotopes in Nb.

| Configuration | Isotope | Energies (eV) |  |  | Displacements (in $a/200$) |  |  |  | P tensor |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  | $\Delta E_0$ | $E_L$ | $\Delta E$ | first neighbor |  | second neighbor |  | TrP (eV) | $3(A-B)/\mathrm{TrP}$ |
|  |  |  |  |  | $u_1$ | $u_2$ | $u_3$ | $u_4$ |  |  |
| 1*T* | H | −0.724 | 0.248 | −0.476 | 6.3 | 2.7 | 0.0 | 0.3 | 10.35 | −0.12 |
|  | D | −0.641 | 0.224 | −0.417 | 6.0 | 2.6 | 0.0 | 0.4 | 9.93 | −0.10 |
|  | T | −0.603 | 0.213 | −0.390 | 5.8 | 2.5 | 0.0 | 0.4 | 9.74 | −0.08 |
| 4*T* | H | −0.727 | 0.304 | −0.423 | 11.6 |  | 0.9 |  | 9.42 | 0.85 |
|  | D | −0.597 | 0.240 | −0.357 | 9.6 |  | 1.4 |  | 9.29 | 0.57 |
|  | T | −0.551 | 0.221 | −0.336 | 8.9 |  | 1.6 |  | 9.14 | 0.49 |
| 6*T* | H | −0.545 | 0.219 | −0.326 | 4.3 |  | 0.4 | 2.9 | 11.64 | −0.04 |
|  | D | −0.476 | 0.194 | −0.282 | 4.0 |  | 0.4 | 2.8 | 11.11 | −0.07 |
|  | T | −0.445 | 0.183 | −0.262 | 3.8 |  | 0.4 | 2.8 | 10.87 | −0.08 |

for all isotopes. It is also noted that the 4*T* configuration is accompanied by a stress field much larger in anisotropy and slightly smaller in magnitude than that of the 1*T* configuration.

The wave functions of hydrogen isotopes and a positive muon in the 1*T* configuration are shown in Fig. 2. In order to illustrate a degree of anisotropy, curves are drawn for three different directions, ⟨100⟩, ⟨110⟩, and ⟨010⟩. Results for a proton in the ⟨010⟩ direction and those of deuterons are omitted for the sake of clarity. The wave functions of hydrogen isotopes in ⟨100⟩ and ⟨110⟩ directions are very close of the ground-state wave functions of harmonic oscillators corresponding to $\Delta E_1 = 0.17$ eV for a proton and $\Delta E_1$'s scaled by the mass ratios for other isotopes.

The wave functions obtained for the 4*T* configuration are shown in Fig. 3. The figure includes the wave function and the energy of the ground state, and profiles of the interaction potential along the line *AA'* shown in the inset. A potential profile in the undistorted lattice is shown in (a), and results for H and $\mu^+$ are shown in (b) and (c), respectively. A drastic change of the potential field caused by the self-trapping distortion of the lattice can be readily noted. A local maximum of the potential originally located at the center (*O* site) is lowered drastically, leaving only a small hump at the bottom of a broad potential well. The wave function is now extended over the broad potential well, and the maxima of its amplitude, reminiscent of the *T* sites in the undistorted lattice, are found to be displaced inward by an appreciable amount.

It may be appropriate here to give a limit of errors in the numerical results. According to some test calculations, the effect of choosing

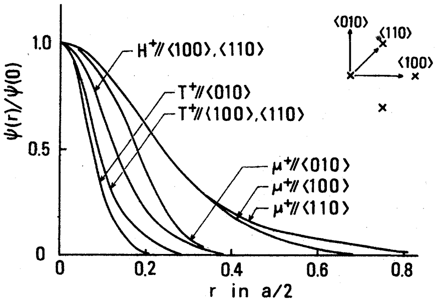

FIG. 2. Ground-state wave functions of a proton, a triton, and a positive muon in the 1*T* configuration in Nb. Variation of the amplitude in some principal directions on the (001) plane is shown. The wave function of a deuteron is omitted for the sake of clarity.

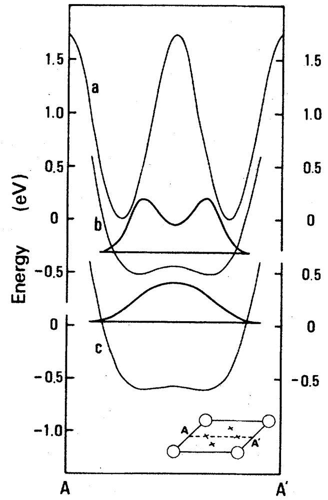

FIG. 3. Potential profiles and ground-state wave functions of a proton and a positive muon in the 4*T* configuration is Nb. Variation along the line *AA'* in the inset is shown. (a) Potential profile in the undistorted lattice, (b) proton, and (c) muon.

finite mesh points and finite regions in which the Schrödinger equation is solved leads to an error of less than 1 meV. Errors arising from cutting off the range of the direct force are roughly estimated at ~3–5 meV. The iteration is terminated when the convergence is attained to within 0.1 meV. Errors due to the use of the approximate potentials have not been assessed.

### B. Positive muons in Nb

Results of the calculation for positive muons in $1T$, $4T$, and $6T$ configurations in Nb are given in Table III. In contrast to the case of hydrogen isotopes, the occupancy of $4T$ sites is energetically most favorable. A potential profile and the wave function for the $4T$ configuration are shown in Fig. 3(c). In this case, a hump of the potential at the center ($O$ site) becomes even smaller due to larger displacements of the nearest-neighbor $M$ atoms, and the wave function has a single maximum centered on the $O$ site. This situation can legitimately be called the $O$-site occupancy. The wave function of a positive muon in the $1T$ configuration is shown in Fig. 2. A small hump in the tail of the ⟨110⟩ direction means that a small part of a muon is extended to the neighboring $T$ sites.

## V. DISCUSSION

### A. Relative stability of $1T$ and $4T(O)$ configurations

One of the most important achievements of the present calculation is that the observed $T$-site occupancy of hydrogen isotopes in Nb is explained quantitatively. In fact, the present treatment can go even further and provide a consistent account of some general trends in the relative stability of the $1T$ and $4T(O)$ configurations.

The variation of the difference in energy of $1T$ and $4T(O)$ configurations with mass of an interstitial is shown in Fig. 4. The result obtained for a hypothetical particle with mass $\frac{1}{2}m_p$ is also included. A tendency that the $4T(O)$ configuration becomes relatively more stable than the $1T$ configuration with decreasing mass can be readily noted. The variation of TrP with mass is also worthy of notice. As shown in Tables II and III, for a given configuration, TrP increases with decreasing mass, indicating that lighter isotopes appear to be larger in size. This trend comes from the contribution of the kinetic energy, and is also reflected in the wave functions: The wave function of a positive muon is more extended than that of a proton as shown in Fig. 2. In this context, it is interesting to recall that larger interstitial atoms (C, N, O, . . . ) occupy $O$ sites without exception. The stabilization of $O$ sites for larger atoms is a result of the drastic lowering of the potential energy with outward displacements of the two nearest-neighbor $M$ atoms. The situation is essentially the same in the present calculation as in the calculation of Johnson *et al.*[31] on N and C in Fe and V.

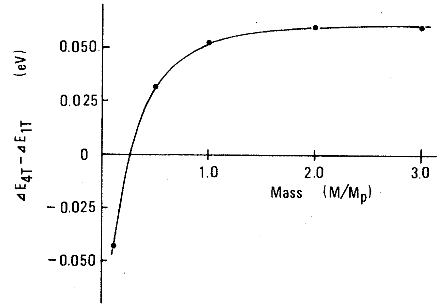

FIG. 4. Variation of the difference of self-trapping energies of $4T$ and $1T$ configurations in Nb with isotope mass.

Parenthetically, it may be pointed out that the self-trapping energy for the $T$-site occupancy (Table II) is much larger in magnitude than Kehr's estimate (0.20 eV).[8,9] It arises from the method of calculating the energy of the interstitial atom: In the harmonic approximation adopted by Kehr, $\Delta E_0$ is always equal to $-2E_L$. In our more rigorous calculations, a lowering of the energy eigenvalue $\Delta E_0$ is found to be much larger in magnitude, and leads to the formation of a more stable self-trapped state.

Regarding the anisotropy of the stress field caused by the $4T(O)$-site occupancy, it may be

TABLE III. Properties of the self-trapped state of positive muons in Nb.

| | | | | Displacements $(a/200)$ | | | | | **P** tensor |
|---|---|---|---|---|---|---|---|---|---|
| | Energies (eV) | | | first neighbor | | second neighbor | | Tr**P** | $3(A-B)/$Tr**P** |
| Configuration | $\Delta E_0$ | $E_L$ | $\Delta E$ | $u_1$ | $u_2$ | $u_3$ | $u_4$ | (eV) | |
| $1T$ | −1.367 | 0.429 | −0.938 | 8.6 | 3.1 | −0.3 | −0.2 | 12.90 | −0.25 |
| $4T$ | −1.435 | 0.454 | −0.981 | 14.4 | | 0.8 | | 11.18 | 0.93 |
| $6T$ | −1.151 | 0.454 | −0.697 | 7.1 | | 3.0 | 0.0 | 15.16 | 0.19 |

noted that the calculated values of $3(A-B)/\mathrm{Tr}\mathbf{P}$ are close to experimental values obtained in those cases where $O$-site occupancy is established; H(D) in $\beta-\mathrm{VH}_x(\mathrm{VD}_x)$ (Table I), and C, N, O in a number of bcc metals.[4] As the tetragonal distortion of the lattice around a $4T(O)$ site is large, it is expected that the presence of uniaxial stress should stabilize $4T(O)$ sites. The expectation is borne out by observations: Near the reaction front of the precipitation of $\beta-\mathrm{V}_2\mathrm{H}$ from $\alpha-\mathrm{VH}_x$ matrix, a tetragonal structure with continuously variable axial ratio has been found,[32] indicating that H atoms move from $1T$ to $4T(O)$ sites according to the magnitude of the uniaxial internal stress. Another evidence is the data of channeling experiments on D atoms in V that they move out of $T$ sites when oxygen atoms are added.[33] The data seem to indicate that D atoms enter $O$ sites in the presence of a large uniaxial stress field around oxygen atoms on $O$ sites.

Effects of varying the lattice parameter and the lattice Green's function on the relative stability of the $1T$ and $4T(O)$ occupancy are examined by using values appropriate for other group-V metals, V and Ta. Results are given in Table IV. Quantities listed are the self-trapping energy of the $1T$ and $4T(O)$ configurations, $\Delta E_{1T}$ and $\Delta E_{4T}$, respectively; their difference, $\Delta E_{1T}-\Delta E_{4T}$; $\mathrm{Tr}\mathbf{P}$ and $3(A-B)/\mathrm{Tr}\mathbf{P}$ of these two configurations. Case 1, which corresponds to H in Nb, is reproduced from Table II to facilitate comparison. In case 2, the lattice Green's function of Nb is replaced by that of Ta, leaving other parameters the same as in case 1. This corresponds to H in Ta. In cases 3–5, the lattice parameter is reduced from 3.3 to 3.0 Å, the value appropriate to V. In cases 3 and 4, the lattice Green's function of Nb is used, whereas in case 5, that of V is used. In cases 1–3, the potential parameters adopted are those given by Eq. (11), whereas in cases 4 and 5, $\rho_1$ and $\rho_2$ are scaled by multiplying by 3.0/3.3. Thus, case 5 corresponds to H in V. As lattice Green's functions of Ta and V, values reported by Tewary[30] have been adopted.

We note that the reduction of the lattice parameter always tends to stabilize the $4T(O)$ occupancy. Thus, the decrease of the size of $M$ atoms acts in the same way as the increase of the size of interstitial atoms. The effect of varying the lattice Green's function can be seen by comparison of cases 1 and 2, and also 4 and 5. The effect is by no means small. Significant to note is the fact that the energy separation between $1T$ and $4T(O)$ configurations becomes much smaller in V as compared to Nb and Ta, as a combined effect of the lattice parameter and the lattice Green's function. This result is consistent with two kinds of experimental observations: First, nearly 10% of D atoms are found to occupy $O$ sites in $\alpha-VD_x$.[34,35] Indeed, an appreciable fraction of D atoms is expected to enter $4T(O)$ sites in thermal equilibrium if the energy separation becomes small. Second, in the phase transition $\alpha\rightarrow\beta$ in $\mathrm{VH}_x$ and $\mathrm{VD}_x$, H(D) atoms are known to move from $T$ sites to $O_z$ sites, in contrast to the case of Nb and Ta, in which H(D) atoms remain in $T$ sites in transition to the ordered phases. Its implication should be that, in V in contrast to Nb and Ta, the cooperative occupancy of $O_z$ sites and concomitant lowering of the energy of $O_z$ configuration more than offset the small-energy separation between $T$ and $O$ configurations in the $\alpha$ phase. In our previous paper,[36] we have shown by more approximate quantum-mechanical calculations that the elongation of one of the cube axes lowers the total energy of $\mathrm{VH}_x$ and $\mathrm{VD}_x$. A more detailed analysis of the problem based on the present formulation will be made in a forthcoming paper.

The variation of the relative stability of the $T$- and $O$-site occupancy with lattice parameter is manifested by the results of channeling experiments. The $O$-site occupancy is found in Cr,[37] and the mixed occupancy in V as described above. These two metals possess much smaller lattice parameters as compared to other bcc metals in

TABLE IV. Self-trapping energy and force-dipole tensor of H atoms in the $1T$ and $4T$ configurations in group-V metals.

| Case | $a$(Å) | Green's function | Potential parameters | Self-trapping energies (eV) | | | **P** tensor | | | | Note |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Tr**P** (eV) | | $3(A-B)/\mathrm{Tr}\mathbf{P}$ | | |
| | | | | $\Delta E_{1T}$ | $\Delta E_{4T}$ | $\Delta E_{1T}-\Delta E_{4T}$ | $1T$ | $4T$ | $1T$ | $4T$ | |
| 1 | 3.3 | Nb | $\rho_1, \rho_2$ | −0.476 | −0.423 | −0.053 | 10.35 | 9.42 | −0.12 | 0.85 | H in Nb |
| 2 | 3.3 | Ta | $\rho_1, \rho_2$ | −0.429 | −0.372 | −0.057 | 10.96 | 10.18 | −0.15 | 0.76 | H in Ta |
| 3 | 3.0 | Nb | $\rho_1, \rho_2$ | −0.429 | −0.385 | −0.044 | 10.13 | 9.11 | −0.11 | 0.87 | |
| 4 | 3.0 | Nb | $(\rho_1, \rho_2)\times 3.0/3.3$ | −0.494 | −0.447 | −0.047 | 10.48 | 9.47 | −0.13 | 0.89 | |
| 5 | 3.0 | V | $(\rho_1, \rho_2)\times 3.0/3.3$ | −0.523 | −0.493 | −0.030 | 10.13 | 8.85 | −0.11 | 0.89 | H in V |

which the $T$-site occupancy is found [Nb,[1,38] Ta,[1,39] W (Ref. 37)]. From these systematics, it seems very probable that H atoms occupy $O$ sites in Fe which has a lattice parameter close to Cr. No experimental data are yet available to verify this conjecture.

### B. State of positive muons

Judging from the systematic variation of energy with mass (Fig. 4), the occupancy of $O$ sites by positive muons in Nb appears rather convincing. In principle, there remains a possibility that the wave function of a muon is so much extended in space that solving a Schrödinger equation within a limited volume may not lead to the most stable configuration. However, this seems rather unlikely. In our calculation on the $1T$ configuration, five $T$ sites are contained within the volume in which the Schrödinger equation is solved, but the wave function is found to have an appreciable amplitude on only one of them at the center (Fig. 2).

An experimental determination of sites occupied by muons could be made from measurements of the depolarization rate of $\mu$SR (muon-spin rotation) at low temperatures where muons are at rest in the lattice. The Van Vleck second moment to be derived from the depolarization rate, as a function of orientation and strength of the external magnetic field, reflects the local environment of muons. Lankford *et al.*[40] have attempted to make an identification of sites by comparing their data of the depolarization rate with the result of their calculation performed on several possible configurations. The configurations they examined include $O$, $1T$, $2T$, $4T$, $5T$, and $6T$, of which a reasonable agreement was obtained for two configurations $2T$ and $4T$. However, it must be pointed out that their estimates of the second moment are not very reliable quantitatively. It is because displacements of surrounding Nb atoms are neglected, and the simultaneous occupation of $N$ tetrahedral sites is approximated by placing $1/N$ of a muon spin on these $N$ sites.

We have calculated the fractional variation of $1/r^6$ for the first- and second-neighbor Nb atoms when the atomic displacement and the finite extension of the wave function of a muon are taken into account. For the $4T(O)$-site occupancy, a fractional change in the Van Vleck second moment in the zero field is then obtained by summing the contributions of the first and second neighbors with weights 0.8 and 0.2, respectively. Results are given in Table V. The effect of the atomic displacement is seen to be very large; it reduces the second moment to 55% of the undistorted lattice. The effect of the finite extension of the wave function is less important in comparison. Since the depolarizaton rate for the $O$-site occupancy has been estimated at 0.70 $\mu s^{-1}$ without including atomic displacements,[40] the value is modified by the present calculation as $0.70\sqrt{0.55} = 0.51\ \mu s^{-1}$. This agrees reasonably well with their experimental value, 0.45 $\mu s^{-1}$. It must be emphasized that the inclusion of atomic displacements is of crucial importance in calculating the second moment. Lankford *et al.*[40] have noted that their results can be interpreted in terms of the $T$-site occupancy provided the displacement of nearest-neighbor Nb atoms is as large as 13%. However, the value is much larger than the present estimate (8.2%, calculated from Table III), and is therefore highly improbable. More detailed comparison with experiments has not been attemped here, because it proved later that the "rigid-lattice" depolarization rate cited above could only be observed in the presence of some intersitial impurities like N and/or O, and accordingly, the observed depolarization rate is the one of muons in some trapped state.

### C. Excited state

The energy separation between the ground state and the excited state of H(D) atoms has been determined by two different methods of the neutron spectroscopy, the energy-gain spectroscopy and the energy-loss spectroscopy. The calculation described in Sec. III deals with the process to be encountered in the energy-loss spectroscopy. In this case, the initial state is the ground state in which the surrounding lattice has been relaxed to the most stable configuration, and this configura-

TABLE V. Van Vleck second moment for positive muons in Nb.

| Atomic displacement | Distribution of $\mu^+$ dipole | Calculated quantity | Contribution of first neighbors | second neighbors | Second moment 0.8 (first neighbor) +0.2 (second neighbor) |
|---|---|---|---|---|---|
| neglected | point | $r^{-6}$ | 1.00 | 1.00 | 1.00 |
| included | point | $r^{-6}$ | 0.45 | 0.96 | 0.55 |
| included | $\mu^+$ wave function | $\langle r^{-3}\rangle^2$ | 0.40 | 1.12 | 0.55 |

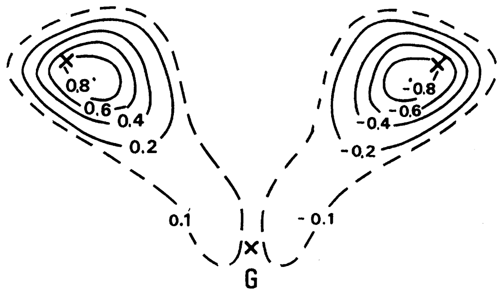

FIG. 5. Wave function of the excited state of a proton which, in its ground state, occupies a $T$ site labeled G in the figure.

tion is assumed to be fixed during the transition. In the case of the energy-gain spectroscopy, on the other hand, the initial state is the excited state with the most stable configuration of the lattice, and the transition takes place to the unrelaxed ground state. The energy separation to be determined from these two experiments are, in general, different. This difference is called the Stokes shift in the optical spectroscopy of polarons. Experimentally, however, no Stokes shift has been found for H(D) atoms in metals within the limit of error of approximately ±10 meV.[2,41] More detailed studies of the Stokes shift by using high-resolution neutron spectrometers are expected to yield useful information on the interaction of H(D) atoms with the surrounding lattice.

Finally, a brief account is given of a spacial aspect of the excited state. In Fig. 5 is shown a contour map of the wave function of the excited state obtained by the calculation described in Sec. III. Rather unexpectedly, the wave function of the excited state has a large amplitude near the neighboring pair of $T$ sites. From this result, it may be inferred that this excited state may serve as one of the possible saddle-point configurations for an elementary jump of a H(D) atom into the next-nearest $T$ site, although this particular path may not be the most efficient one.

In any case, it must be obvious that a quantum-mechanical approach as described here is indispensable in elucidating the nature of excited states as well as migration processes. These problems are now being studied, and will be reported in forthcoming publications.

## VI. CONCLUSIONS

From quantum-mechanical calculations dealing specifically with hydrogen isotopes and positive muons in Nb, a consistent account is given of various properties of the self-trapped state of light interstitial atoms. They include the following: the type of interstitial sites occupied, the relative stability of the $1T$ vs $4T(O)$-site occupancy, its dependence on isotope mass and the lattice parameter of the matrix, the distortion of the surrounding lattice, etc. The $O$-site occupancy is predicted for positive muons in Nb. Some properties of the excited state are also clarified, including its wave function and its relevance to the migration process.

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[3] See, e.g., H. Peisl, in Ref. 2, p. 53.

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