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Atomic-hydrogen impurities in solid molecular hydrogen

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The dynamic-local-field approximation has been modified to accommodate dilute atomic-H impurities in solid H_2. The impurities are assumed to occupy substitutional sites. Calculated properties of the atomic impurities include the single-particle-distribution function, the root-mean-square fluctuations about the equilibrium position, and the lattice distortion.

I. INTRODUCTION

There has recently been considerable interest in producing and storing atomic hydrogen in bulk quantities.[1] One approach, taken by Webeler,[2,3] involves the generation of atomic hydrogen within a molecular-hydrogen lattice by tritium decay. These experiments have all been at low concentrations of atomic hydrogen. The purpose of this study was to investigate such systems using an appropriately modified dynamic-local-field approximation.[4] The model used allows for the distortion in the lattice around the atomic-hydrogen impurity. Some studies of defects in other quantum solids[5-11] predict that point defects would be nonlocalized "defectons." This work, however, treats the hydrogen atom as a localized defect in a manner similar to previous studies for ^{3}He and ^{4}He.[12-17] An important assumption in this study is that the hydrogen-atom impurity occupies a substitutional site. The electron-spin-resonance experiments of Adrian[18] support this view for atomic hydrogen in a molecular-hydrogen lattice. For simplicity, calculations assumed a face-centered-cubic lattice instead of the actual hexagonal-close-packed structure.

II. THEORY

The energy of a molecular-hydrogen lattice containing a single hydrogen-atom impurity was calculated variationally. The starting point was the dynamic-local-field approximate calculation of the ground-state energy of an all-molecular-hydrogen lattice.[19] For an all-molecular-hydrogen calculation, the variational wave function of the N-particle system is assumed to have the form

$$\Phi(\vec{r}_1,\ldots,\vec{r}_N)=\prod_{i=1}^{N}\phi_{H_2}(\vec{r}_i-\vec{R}_i)\prod_{j<k}^{N}f_{H_2\text{-}H_2}(r_{jk}), \quad (1)$$

where the $\phi(\vec{r}_i-\vec{R}_i)$ localize the particles around their equilibrium lattice sites $\{\vec{R}_i\}$ and the $f_{H_2\text{-}H_2}$ account for the important short-ranged pair correlations. Parametrized forms are chosen for ϕ and f, and the parameters are determined by minimizing the expectation value of the free energy.

With a single hydrogen-atom impurity introduced into the system, the total wave function is assumed to have the form

$$\Phi(\vec{r}_1,\ldots,\vec{r}_N)=\phi_H(\vec{r}_1)\prod_{i=2}^{N}\phi_{H_2}(\vec{r}_2)\times\prod_{j=2}^{N}f_{H\text{-}H_2}(r_{1j})\prod_{j<k=2}^{N}f_{H_2\text{-}H_2}(r_{jk}), \quad (2)$$

where the subscripts H and H_2 refer to the hydrogen atom and molecule, respectively. The position $\vec{r}_1$, will always locate the H atom. The quantities in Eq. (2) are chosen to be of the form

$$\phi_H(r_1)=(\beta_H/\pi)^{3/4}\exp[-\tfrac{1}{2}\beta_H(\vec{r}_1-\vec{R}_1)^2], \quad (3)$$

$$\phi_{H_2}(r_i)=(\beta_{H_2}/\pi)^{3/4}\exp[-\tfrac{1}{2}\beta_{H_2}(\vec{r}_i-\vec{R}_i)^2], \quad (4)$$

$$f_{H\text{-}H_2}(r_{1j})=\exp[\tfrac{1}{2}(k_H/r_{1j})^5], \quad (5)$$

$$f_{H_2\text{-}H_2}(r_{jk})=\exp[-\tfrac{1}{2}(k_{H_2}/r_{jk})^5], \quad (6)$$

where ϕ_{H_2} and $f_{H_2\text{-}H_2}$ play the same role as in Eq. (1), ϕ_H localizes the H atom around $\vec{R}_1$, and $f_{H\text{-}H_2}$ accounts for the short-ranged pair correlations between the atom and the molecules. There are four variational parameters in the wave function, β_H, β_{H_2}, k_H, and k_{H_2}. These and the nearest-neighbor bond length of the H atom make five variational parameters. In order to simplify the problem β_{H_2} and k_{H_2} are assumed to have values corresponding to the ground state of the all-molecular-hydrogen lattice. These values are 1.714 Å^{-2} and 3.282 Å, respectively.[19] This reduces the calculation to a manageable one with three variational parameters.

The Hamiltonian for the system is

$$H=-\frac{\hbar^2}{2m_H}\nabla_1^2-\frac{\hbar^2}{2m_{H_2}}\sum_{i=2}^{N}\nabla_i^2+\sum_{j=2}^{N}V_{H\text{-}H_2}(r_{1j})+\sum_{j<k=2}^{N}V_{H_2\text{-}H_2}(r_{jk}), \quad (7)$$

where $V_{H_2\text{-}H_2}$ is the interaction potential between two molecules[19] and $V_{\mathrm{H}\text{-}\mathrm{H}_2}$ is the interaction potential between a hydrogen atom and a hydrogen molecule. The $V_{\mathrm{H}\text{-}\mathrm{H}_2}$ potentials used in this study are those of Gengenback *et al.*[20] They fit the most recent experimental data with a Born-Mayer potential in the repulsive region, a cubic Spline fit in the well region, and a van der Waals form for the long-range region. It is appropriately labeled the Born-Mayer–Spline–van der Waals potential. The well depth for this potential is 27.15 K, compared with 32.6 K for $V_{\mathrm{H}_2\text{-}\mathrm{H}_2}$.

Using Eqs. (2)–(7) and some manipulation (similar to the development in Ref. 4), we can put the expectation value of the Hamiltonian of the system in for form

$$\langle H\rangle=\frac{3\hbar^2\beta_{\mathrm{H}}}{4m_{\mathrm{H}}}+\frac{(N-1)3\hbar^2\beta_{\mathrm{H}_2}}{4m_{\mathrm{H}_2}}+\langle\Phi_{\mathrm{H}}\,|\,\Phi_{\mathrm{H}}\rangle^{-1}\times\int|\phi_{\mathrm{H}}|^2\left(\sum_{j=2}^{N}\nu_{\mathrm{H}}(r_{1j})+\sum_{\substack{\lambda<k\\ \lambda\geq 2}}^{N}\nu_{\mathrm{H}_2}(r_{\lambda k})\right)d\vec{\mathrm{r}}_1\cdots d\vec{\mathrm{r}}_N\,, \tag{8}$$

where

$$\nu_{\mathrm{H}}(r_{ij})=V_{\mathrm{H}\text{-}\mathrm{H}_2}(r_{ij})-\frac{\hbar^2}{4\mu}\nabla_1^2\ln f_{\mathrm{H}\text{-}\mathrm{H}_2}(r_{ij}), \tag{9}$$

$$\nu_{\mathrm{H}_2}(r_{\lambda k})=V_{\mathrm{H}_2\text{-}\mathrm{H}_2}(r_{\lambda k})-\frac{\hbar^2}{2m_{\mathrm{H}_2}}\nabla_K^2\ln f_{\mathrm{H}_2\text{-}\mathrm{H}_2}(r_{\lambda k})\,, \tag{10}$$

and μ is the reduced mass.

In the dynamic-local-field approximation Eq. (8) becomes

$$\langle H\rangle=\frac{3\hbar^2\beta_{\mathrm{H}}}{4m_{\mathrm{H}}}+\frac{(N-1)3\hbar^2\beta_{\mathrm{H}_2}}{4m_{\mathrm{H}_2}}+\langle\Phi_{\mathrm{H}}|\Phi_{\mathrm{H}}\rangle^{-1}\left(\sum_{j=2}^{N}\int\phi_{\mathrm{H}}^2(\vec{\mathrm{r}}_1)\phi_{\mathrm{H}_2}^2(\vec{\mathrm{r}}_j)f_{\mathrm{H}\text{-}\mathrm{H}_2}(r_{1j})\nu_{\mathrm{H}}(r_{1j})G_{\mathrm{H}}(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_j)d\vec{\mathrm{r}}_1\,d\vec{\mathrm{r}}_j+\sum_{\substack{\lambda<k\\ \lambda\geq 2}}^{N}\int\phi_{\mathrm{H}_2}^2(\vec{\mathrm{r}}_\lambda)\phi_{\mathrm{H}_2}^2(\vec{\mathrm{r}}_k)f_{\mathrm{H}_2\text{-}\mathrm{H}_2}^2(r_{\lambda k})\nu_{\mathrm{H}_2}(r_{\lambda k})G_{\mathrm{H}_2}(\vec{\mathrm{r}}_\lambda,\vec{\mathrm{r}}_k)d\vec{\mathrm{r}}_\lambda d\vec{\mathrm{r}}_k\right)\,, \tag{11}$$

where $G_{\mathrm{H}_2}(\vec{\mathrm{r}}_\lambda,\vec{\mathrm{r}}_k)$ is the same as in Eq. (12) of Ref. 4,

$$G_{\mathrm{H}_2}(\vec{\mathrm{r}}_\lambda,\vec{\mathrm{r}}_k)=\prod_{s\neq\mathrm{NN}\lambda}{}'f_{\mathrm{H}_2\text{-}\mathrm{H}_2}^2(\vec{\mathrm{r}}_\lambda-\vec{\mathrm{R}}_s)\prod_{\rho\neq\mathrm{NN}k}{}'f_{\mathrm{H}_2\text{-}\mathrm{H}_2}^2(\vec{\mathrm{r}}_k-\vec{\mathrm{R}}_\rho)\prod_{i=\mathrm{NN}\lambda}{}'M_i(\vec{\mathrm{r}}_\lambda)\prod_{j=\mathrm{NN}k}{}'M_j(\vec{\mathrm{r}}_k)\prod_{l=\mathrm{NN}\lambda k}{}'N_l(\vec{\mathrm{r}}_\lambda,\vec{\mathrm{r}}_k)\,, \tag{12}$$

where the primes indicate that the product is not to include index λ or k, NNλ represents the nearest neighbors to particle λ, NNλk represents the nearest neighbors to both particles λ and k,

$$M_j(\vec{\mathrm{r}}_k)=\int f_{\mathrm{H}_2\text{-}\mathrm{H}_2}^2(r_{kj})\phi_{\mathrm{H}_2}^2(\vec{\mathrm{r}}_j-\vec{\mathrm{R}}_j)d\vec{\mathrm{r}}_j\,, \tag{13}$$

$$N_l(\vec{\mathrm{r}}_\lambda,\vec{\mathrm{r}}_k)=\int f_{\mathrm{H}_2\text{-}\mathrm{H}_2}^2(r_{\lambda l})f_{\mathrm{H}_2\text{-}\mathrm{H}_2}^2(r_{kl})\phi_{\mathrm{H}_2}^2(\vec{\mathrm{r}}_l-\vec{\mathrm{R}}_l)d\vec{\mathrm{r}}_l\,, \tag{14}$$

and

$$G_{\mathrm{H}}(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_j)=\prod_{s\neq\mathrm{NN}1}{}'f_{\mathrm{H}\text{-}\mathrm{H}_2}^2(\vec{\mathrm{r}}_1-\vec{\mathrm{R}}_s)\prod_{p\neq\mathrm{NN}k}{}'f_{\mathrm{H}_2\text{-}\mathrm{H}_2}^2(\vec{\mathrm{r}}_k-\vec{\mathrm{R}}_\rho)\prod_{\substack{i=\mathrm{NN}1\\ \neq\mathrm{NN}k}}{}'\int f_{\mathrm{H}\text{-}\mathrm{H}_2}^2(\vec{\mathrm{r}}_{1i})\phi_{\mathrm{H}_2}^2(\vec{\mathrm{r}}_i-\vec{\mathrm{R}}_i)d\vec{\mathrm{r}}_i\times\prod_{\substack{j=\mathrm{NN}k\\ =\mathrm{NN}\lambda}}{}'\int f_{\mathrm{H}_2\text{-}\mathrm{H}_2}^2(\vec{\mathrm{r}}_{kl})\phi_{\mathrm{H}_2}^2(\vec{\mathrm{r}}_j-\vec{\mathrm{R}}_j)d\vec{\mathrm{r}}_j\prod_{l=\mathrm{NN}1k}\int f_{\mathrm{H}\text{-}\mathrm{H}_2}^2(\vec{\mathrm{r}}_{1l})f_{\mathrm{H}_2\text{-}\mathrm{H}_2}^2(\vec{\mathrm{r}}_{kl})\phi_{\mathrm{H}_2}^2(\vec{\mathrm{r}}_l-\vec{\mathrm{R}}_l)\,d\vec{\mathrm{r}}_l\,. \tag{15}$$

In evaluating Eq. (11) as a function of the three variational parameters, several approximations were necessary. First, the products in Eq. (14) included only the first and second nearest neighbors to 1 and k. This approximation was also made for other dynamic-local-field approximation calculations in a face-centered-cubic lattice, and introduces negligible error. Second, the distortion in the lattice was assumed to affect only the distances between the hydrogen impurity and its first nearest neighbors and the distances between the atom's first nearest neighbors and those fourth nearest neighbors which are in the same direction from the atom as the lattice distortion.

Consider the effect of the lattice distortion on the nearest neighbors to the impurity. Let the energy change per molecule of these nearest neighbors, from their value for a pure H_2 solid, be ΔE_1. Clearly, the impurity distortion will change the equilibrium distances between this molecule and all of its neighbors. Here ΔE_1 is calculated by neglecting all but two of these distance changes. A careful look at how the distances change shows why this approximation is justified. As the nearest-neighbor molecule moves away from the atom it moves directly toward one of the atom's fourth nearest neighbors. Two distance changes are obviously important. They are the change in bond length with the atom and with the fourth nearest neighbor. The molecule also moves closer to four of its nearest neighbors, which form the base of a square bipyramid, with the molecule in question and one in the fourth nearest-neighbor shell as the apex molecules. However, the change in distance between the molecule and these four neighbors is approximately a factor of 2 less than the incremental change in the distance from the molecules to the atom's fourth nearest neighbor. This, plus the fact that the molecule, while moving toward four molecules, is also moving away from other nearest neighbors, tends to negate the importance of bond-length changes for nearest-neighbor molecules other than the two previously mentioned. The energy change for the fourth nearest neighbors to the atom, ΔE_4, is based on similar reasoning. The only bond-length changes are assumed to be with the atom and with its first nearest neighbor. Finally, all second, third, and molecules beyond fourth nearest neighbors are assumed to have the same energy per molecule as in an all-H_2 lattice.

The predominant change in the lattice energy is due to the substitutional replacement of an H_2 molecule by an H atom. This energy change we call ΔE_{H}, which is the difference in energy between that of the H atom, E_{H}, and that of an H_2 molecule, E_{H_2}:

$$E_{\mathrm{H}} = \frac{3\hbar^2}{2m_{\mathrm{H}_2}} + \frac{1}{2}\left\langle \sum_{j=2}^{N} v_{\mathrm{H}}(r_{1j}) \right\rangle . \tag{16}$$

Two additional quantities were calculated: the single-particle distribution function $R(|\vec{r}_1 - \vec{R}_1|)$ and the root-mean-square fluctuation about the equilibrium position for the hydrogen atom, $\langle(\vec{r}_1 - \vec{R}_1)^2\rangle^{1/2}$. The equations used are similar to Eq. (16) in Ref. 4.

III. RESULTS AND DISCUSSION

The quantity of interest is not the actual energy of the crystal given by Eq. (11), since this quantity depends on the crystal size. For this study the results will be given in terms of the difference in energy, ΔE, of a crystal with one atom of hydrogen and $N-1$ hydrogen molecules and a crystal composed of N hydrogen molecules. For the all-molecular-hydrogen calculation the results were reported in terms of an energy per molecule.[19] Note that when this is done, two-body contributions to the energy, like the interaction potential, are divided equally between molecules. Thus, ΔE is made up of (*i*) ΔE_{H}, the "energy" of the hydrogen atom, E_{H}, minus the "energy" of a hydrogen molecule in an all-molecular-hydrogen lattice, E_{H_2}; (ii) the difference in energy between the "energy" of the 12 molecules in the atom's first nearest-neighbor shell and the 12 molecules in an all-molecular-hydrogen lattice, ΔE_1; and (iii) similar terms ΔE_2, ΔE_3, etc., for each successive shell of neighbors to the hydrogen atom. In this work,

$$\Delta E = \Delta E_{\mathrm{H}} + \Delta E_1 + \Delta E_4 . \tag{17}$$

When the contributions to ΔE are separated in this manner, all of the contributions to ΔE at equilibrium are positive. That is, all of the terms tend to increase the energy of the lattice with a

TABLE I. Variational results. $\sigma = 2.958$ Å

β_{H} (σ^{-2})	k_{H} (σ)	P $R_{NN,\mathrm{rel}}/R_{NN,\mathrm{unrel}}$	ΔE (K)	ΔE_{H} (K)	ΔE_1 (K)	ΔE_4 (K)
18.0	1.07	1.00	147.71	106.00	44.45	-3.74
15.5	1.06	1.03	132.01	83.73	42.26	6.02
13.5	0.97	1.06	129.37	67.75	44.92	16.70
13.5	1.01	1.06	127.11	66.83	43.64	16.64
13.5	1.05	1.06	128.16	67.25	44.34	16.56
13.5	0.93	1.06	133.97	69.98	47.23	16.76
15.0	0.93	1.06	133.06	73.90	43.71	15.45
16.5	0.93	1.06	133.05	78.15	40.64	14.26
18.0	0.93	1.06	133.72	82.63	37.93	13.16
15.0	1.02	1.06	122.64	72.88	38.47	11.29
13.0	0.97	1.09	132.04	59.02	46.89	26.13
12.0	0.93	1.12	141.63	52.70	53.26	35.67

hydrogen-atom impurity compared to the all-molecular-hydrogen lattice. The largest contribution comes from $\Delta E_{\mathrm{H}} = E_{\mathrm{H}} - E_{\mathrm{H}_2}$. This term is large and positive, which is not unexpected, since the H-H_2 potential has a shallower well and is more repulsive than the H_2-H_2 potential. Moreover, the lower atomic mass leads to a higher kinetic energy for the H atom. The magnitude of all of these terms depends on the values of the three variational parameters. Table I is a partial list of some representative values obtained in this study. A total of over 70 points was used, giving some indication of the difficulty of minimizing a function with respect to three separate variational parameters.

The minimum in energy occurs for values of the variational parameters β_{H}, k_{H}, and P of 1.714 Å^{-2}, 3.017 Å, and 1.060, where P is the ratio of the relaxed to the unrelaxed nearest-neighbor distance. The total difference in energy, compared with that of the all-molecular-hydrogen lattice, ΔE, at this point is 122.6 K. The energy of the hydrogen atom is $E_{\mathrm{H}} = -15.9$ K. This energy is defined by Eq. (16) and is the analog of the binding energy of a pure lattice. This compares with a value of $E_{\mathrm{H}_2} = -88.8$ K.

One of the interesting results of this study is the rather large 6.0% distortion in the nearest-neighbor distance. Similar studies[12-17] for ^{3}He in ^{4}He found distortions between 0.5 and 2.2%. The distortion for H in H_2 was expected to be larger than for ^{3}He in ^{4}He because of the greater difference in mass, but this alone would not account for such a large change. The large repulsive core of the H-H_2 potential is one factor contributing to this large distortion. Another arises because of the more accurate ground-state expectation values obtained in this study compared with previous calculations.[12-17] Many of those calculations were based on Nosanow's[21] cluster expansion techniques, but as pointed out by Hetherington,[5] the deficiencies of the method were the weakest point in his study. In fact an application of the techniques of this study to a ^{4}He matrix containing a ^{3}He defect shows a nearest-neighbor bond-length distortion of more than 3% around the ^{3}He atom.

Figure 1 contains plots of the single-particle distribution function for a hydrogen molecule in an all-molecular lattice and for a hydrogen atom in a similar lattice. For purposes of comparison this figure also contains the single-particle distribution function for ^{3}He and ^{4}He. The coordinate r is in units of σ, which is chosen to have a value of 2.958 Å for all of these plots. The single-particle distribution function for H is only slightly wider than that for H_2, a result consistent with the calculated root-mean-square fluctuations of 0.785 and 0.730 Å, respectively. At first this result appears surprising. With the much lighter mass and shallower interaction potential, it might be expected that the single-particle distribution function for H would be much wider than for H_2. A look at Fig. 2, which contains the interaction potentials for H-H_2 and H_2-H_2, indicates why this does not occur. The relatively narrow H-H_2 potential well acts to localize the H-atom impurity, thus counteracting an opposite tendency induced by the zero-point energy. The small change in root-mean-square fluctuation is also consistent with Varma's[17] conclusion for defects in quantum crystals, which was that "the force-constant changes act to screen the impurity." Specifically for his study of ^{4}He impurities in ^{3}He he states that "the mean-square displacement of the ^{4}He atom is brought closer to that of the ^{3}He atoms."

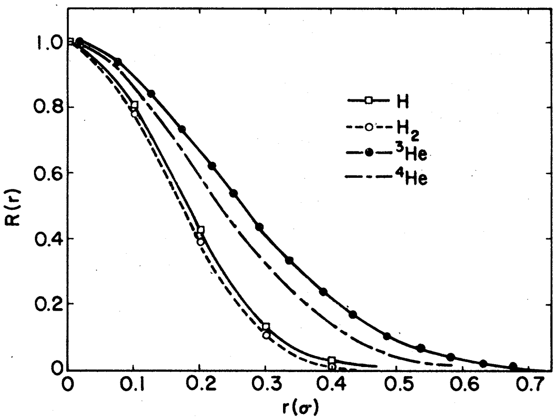

FIG. 1. Single-particle distribution functions for H in H_2, ^{3}He, and ^{4}He.

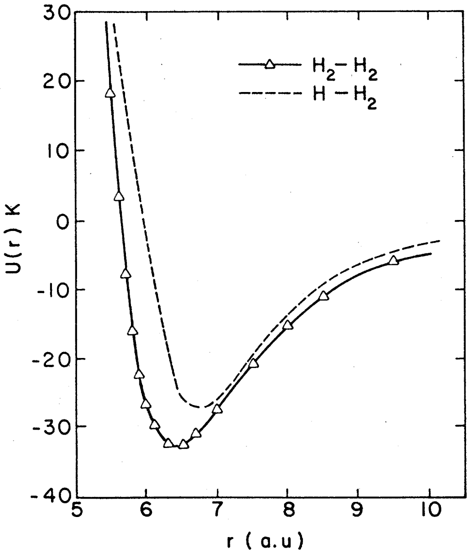

FIG. 2. H-H_2 and H_2-H_2 interaction potentials.

The most significant finding of this study is that, even with a root-mean-square fluctuation about equilibrium comparable to that of an H_2 molecule, the atomic-H impurity causes a significant strain field to develop. The large distortion in the nearest-neighbor bond is felt to be due primarily to the relatively wide repulsive core in the H-H_2 potential compared with the H_2-H_2 potential, and of course to the lighter H mass. Any studies involving a significant concentration of H in the H_2 will be quite complicated owing to the necessity of including these large distortions around the H defects.

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