

## Excited States of Solid Ar:H†

THOMAS H. KEIL AND ALBERT GOLD

*Institute of Optics, University of Rochester, Rochester, New York*

(Received 13 May 1964)

Excitation energies for the 1s-2p and 1s-2s transitions of a hydrogen atom as a substitutional impurity in solid argon have been calculated as a function of nearest-neighbor distance. A tight-binding treatment using Schmidt-orthogonalized wave functions is used to obtain the first-order shift from the atomic absorption energies. Overlap of atomic wave functions is taken into account through terms of second order, and three-center contributions are evaluated explicitly. The additional changes in the energies due to van der Waals interactions are obtained by a variational technique. Excitation energies for the 1s-2p and 1s-2s transitions are found to be  $10.6 \pm 0.2$  and  $12.3 \pm 0.2$  eV, respectively, for a nearest-neighbor distance of  $7.0a_0$ . The former gives good agreement with recent experimental observations.

### I. INTRODUCTION

THE higher excited states of excitons<sup>1</sup> and impurities<sup>2</sup> in solid rare-gas crystals seem to be well understood in terms of the familiar hydrogenic effective-mass model. One expects this model to be less useful for the lowest exciton states, and indeed experimental evidence seems to confirm this suspicion. No wholly satisfactory theory yet exists for the description of these lowest excitations in the relatively "tightly-bound" systems, or for the similar problem of low-lying impurity states. The present paper presents a Heitler-London calculation for the lowest excited states of atomic hydrogen as a substitutional impurity in solid argon. The first-order energy is computed with the help of a Schmidt orthogonalization procedure as discussed by Gold.<sup>3</sup> The van der Waals energy is evaluated using a variational technique due to Buckingham.<sup>4</sup> Very good agreement between the 1s-2p excitation energy, computed for plausible values of the nearest-neighbor separation, and the experimental work of Baldini,<sup>5</sup> strongly supports the validity of the tight-binding model as applied to the description of low-lying states of impurities and excitons in the crystalline noble gases.

### II. THEORY

Following Ref. 3, the total electronic wave functions for the system, consisting of a single hydrogen atom in an argon crystal, in the ground and excited states, respectively, are taken to be

$$\Psi_0 = \alpha \psi_H(\mathbf{r}_H, \sigma_H) \prod_{I \neq H} \prod_i \psi_{Ii}(\mathbf{r}_{Ii}, \sigma_{Ii}); \quad (1a)$$

$$\Psi = \alpha \bar{\psi}_H(\mathbf{r}_H, \sigma_H) \prod_{I \neq H} \prod_i \psi_{Ii}(\mathbf{r}_{Ii}, \sigma_{Ii}). \quad (1b)$$

Here  $\psi_H(\mathbf{r}_H, \sigma_H)$  is the ground-state one-electron function for the hydrogen electron,  $\psi_{Ii}(\mathbf{r}_{Ii}, \sigma_{Ii})$  is the

† Research supported in part by the National Science Foundation.

<sup>1</sup> G. Baldini, Phys. Rev. **128**, 1562 (1962).

<sup>2</sup> G. Baldini and R. S. Knox, Phys. Rev. Letters **11**, 127 (1963).

<sup>3</sup> A. Gold, Phys. Rev. **124**, 1740 (1961).

<sup>4</sup> R. A. Buckingham, Proc. Roy. Soc. (London) **A160**, 94, 113 (1937).

<sup>5</sup> G. Baldini, preceding paper, Phys. Rev. **136**, A248 (1964).

ground-state one-electron function for the  $i$ th electron centered at the  $I$ th argon nucleus.  $\alpha$  is the usual antisymmetrization operator. The excited-state hydrogen function is denoted by  $\bar{\psi}_H$  and is given by

$$\bar{\psi}_H = (\bar{\phi}_H - \sum_{Ii} S_{H,Ii} \psi_{Ii}) [1 - \sum_{Ii} (S_{H,Ii})^2]^{-1/2}. \quad (2)$$

In (2)  $\bar{\phi}_H$  is the free-atom hydrogen wave function for the excited state, and the  $S_{H,Ii}$  are the overlap integrals

$$S_{H,Ii} = \int \bar{\phi}_H \psi_{Ii} d\tau - \delta_{HI}. \quad (3)$$

Hence,  $\bar{\psi}_H$  is orthogonal to the  $\psi_{Ii}$ , and the total wave function (1b) is normalized. The essential assumption made is that overlap of the ground-state impurity wave function with the host wave functions, and also "host-host" overlaps, make a negligible contribution to the excitation energy. Numerical estimates confirm this expectation. The assumptions and approximations involved in this procedure are more fully discussed in Ref. 3.

In the following,  $\psi_H$  is always taken to be the atomic 1s hydrogen function and the  $\psi_{Ii}$ , the solutions of the atomic Hartree-Fock equations for the ground state of the free argon atom.<sup>6</sup>

The first-order excitation energy is given (through terms of second order in overlap quantities) by<sup>3</sup>

$$\Delta E = E_{at} + E_C + E_X + E_T, \quad (4a)$$

where

$$E_{at} = (1/N) \bar{E}_H - E_H - (1/N) \sum_{I \neq H} \sum_i (S_{H,Ii})^2 E_{Ii}, \quad (4b)$$

$$E_C = \frac{1}{N} \left\{ \int |\bar{\phi}_H|^2 C^H d\tau + \sum_{I \neq H} (S_{H,Ii})^2 \int |\psi_{Ii}|^2 \right. \\ \left. \times \left( C^{HI} + \frac{e^2}{|\mathbf{R}_H - \mathbf{r}_{Ii}|} \right) d\tau \right\} - \int |\phi_H|^2 C^H d\tau, \quad (4c)$$

<sup>6</sup> D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).

$$E_X = - \sum_{I \neq H} \sum_i \left[ \frac{1}{N} (\bar{H}, Ii | g | Ii, \bar{H}) - (H, Ii | g | Ii, H) \right], \quad (4d)$$

$$E_T = - \frac{2}{N} \sum_{I \neq H} \sum_i S_{H, Ii} \int \bar{\phi}_H \times \left( C^{HI} + \frac{e^2}{|\mathbf{R}_H - \mathbf{r}_H|} \right) \psi_{Ii} d\tau. \quad (4e)$$

In Eqs. (4)  $E_{at}$  is an atomic excitation energy plus a correction term due to overlap.  $N = [1 - \sum_{Ii} (S_{H, Ii})^2]$ ;  $\bar{E}_H$  and  $E_H$  are, respectively, the excited and ground-state energies of the hydrogen atom, and  $E_{Ii}$  the one-electron Hartree-Fock eigenvalues for the host electrons.  $E_C$  is the so-called "Coulomb overlap" energy.  $C^H$  is the classical electrostatic potential in the crystal with the hydrogen atom removed,  $C^{HI}$  is that with the impurity and the  $I$ th host atom gone, and  $\mathbf{R}_H$  and  $\mathbf{r}_H$  are the coordinates of the hydrogen nucleus and electron, respectively.  $E_X$  is the exchange contribution, and the matrix elements appearing are the usual exchange integrals containing excited or ground-state hydrogen functions as dictated by the presence or absence of a bar.  $E_T$  is a "three-center" term, and, like the others, is more completely discussed in Ref. 3.

The dipole-dipole part of the second order, or van der Waals, energy between a pair of atoms is given (neglecting interatomic exchange and overlap) by<sup>4</sup>

$$E_{d-d} = -C_{12}/R_{12}^6, \quad (5)$$

where

$$C_{12} = - \sum_{i1} \sum_{j2}^4 \{ (R^2)_{1i} (R^2)_{2j} / [(R^2)_{1i} + (R^2)_{2j}] \}, \quad (6)$$

with

$$(R^2)_{Kk} = (Kk | r^2 | Kk) - \sum_{k' \neq k} [(Kk | x | Kk')^2 + (Kk | y | Kk')^2 + (Kk | z | Kk')^2]. \quad (7)$$

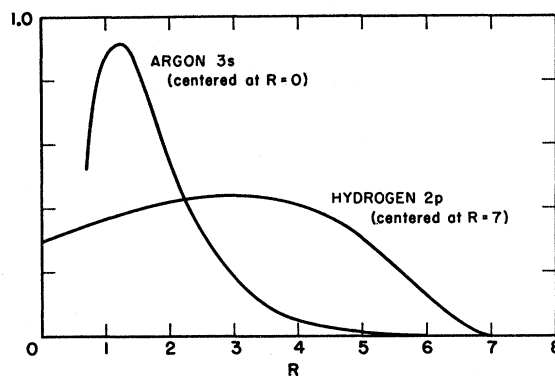


FIG. 1. Plot of  $r$  times the radial wave function for Ar 3s and H 2p.

In (5)  $R_{12}$  is the internuclear separation of the pair, and in the matrix elements of (7)  $r$ ,  $x$ ,  $y$ , and  $z$  retain their usual meaning as coordinates measured from the nucleus of atom K. This expression is summed over the crystal for hydrogen in its ground and excited states to obtain the van der Waals contribution to the excitation energy in a manner previously described.<sup>7</sup> Neglect of overlap and exchange in the second-order contributions is a minor approximation since the second-order energy is already only 5–10% of  $\Delta E$ , and overlap and exchange effects give at most a 10% change in the second-order terms.

### III. RESULTS AND DISCUSSION

Numerical computations for the  $1s-2p$  and  $1s-2s$  excitation energies of Ar:H have been carried out with the aid of Fortran programs<sup>8</sup> written for the University of Rochester IBM-7074 computer. All two- and three-center integrals were evaluated numerically using Löwdin's alpha-function technique.<sup>9</sup> Calculations were carried through for nearest-neighbor distances of 6.0, 7.0, and  $8.0a_0$ .

The normal lattice constant of argon at absolute zero is  $7.1a_0$ . Because of the smallness and relative "softness"

TABLE I. Hydrogen-argon overlap integrals. Separations are in  $a_0$ , and the interatomic axis is taken as the  $z$  direction.

	$R$ ( $a_0$ )	Ar 1s	Ar 2s	Ar 3s	Ar 2px	Ar 2pz	Ar 3px	Ar 3pz	$N$
H 2s	4.0	-0.005	0.041	-0.210	0.000		-0.016		...
	6.0	-0.004	0.031	-0.173	-0.003		0.069		0.488
	7.0	-0.003	0.024	-0.137	-0.003		0.073		0.699
	8.0	-0.002	0.017	-0.104	-0.002		0.066		0.832
	10.0	-0.001	0.008	-0.054	-0.001		0.042		...
	12.0	-0.000	0.004	-0.026	-0.000		0.023		...
H 2p	4.0	0.010	-0.083	0.397	-0.002	0.002	0.039	-0.150	...
	6.0	0.006	-0.046	0.257	-0.006	0.003	0.137	-0.091	0.488
	7.0	0.004	-0.033	0.194	-0.005	0.002	0.126	-0.062	0.733
	8.0	0.003	-0.023	0.138	-0.003	0.001	0.099	-0.038	0.860
	10.0	0.001	-0.011	0.067	-0.002	0.000	0.056	-0.015	...
	12.0	0.000	-0.004	0.036	-0.001	0.000	0.030	-0.005	...

<sup>7</sup> A. Gold, Phys. Chem. Solids 18, 218 (1961).

<sup>8</sup> T. H. Keil, University of Rochester, 1963 (unpublished).

<sup>9</sup> P. O. Löwdin, Advan. Phys. 5, 1 (1956).

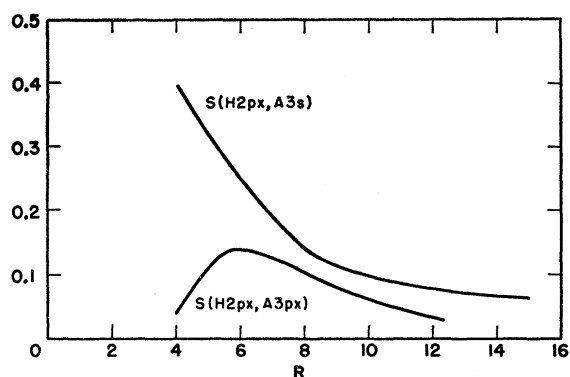


FIG. 2. Typical hydrogen-argon overlap integrals.

of hydrogen in its ground state and because of the close-packed nature of the lattice, it would be expected that the relaxation about the hydrogen atom in its ground state will be about the same as the relaxation about a vacancy. According to Kanzaki,<sup>10</sup> the nearest neighbors about a vacancy in solid argon will move inward the order of 1% of the lattice constant. Thus  $7.0a_0$  is likely a rather good estimate of the nearest-neighbor distance for Ar:H, and excitation energies calculated at that value should be regarded as those theoretically "predicted." In any event, the final result is relatively insensitive to small variations of distance in this region.

Figure 1 shows a plot of  $r$  times the radial wave function for an argon  $3s$  function centered at  $R=0$ , and a hydrogen  $2p$  function centered at  $R=7.0$ . Table I lists the values of the overlap integrals for the hydrogen  $2p$

TABLE II. Contributions to Ar:H  $1s-2p$  excitation energy as a function of nearest-neighbor distance. Numbers without explicitly quoted error are correct to the number of significant figures given.

Term	Nearest-neighbor distance ( $a_0$ )		
	6.0	7.0	8.0
$E_{at}$	43.3	21.5	15.0
$E_C$	-20.1	-6.7	-3.6
$E_X$	-21.6	-7.5	-3.3
$E_T$	$11.5 \pm 0.5$ eV	$3.7 \pm 0.2$ eV	$1.4 \pm 0.1$ eV
$E_{d-d}$	$-1.1 \pm 0.1$ eV	-0.5	-0.2
$E$	$12.0 \pm 0.6$ eV	$10.6 \pm 0.2$ eV	$9.4 \pm 0.1$ eV

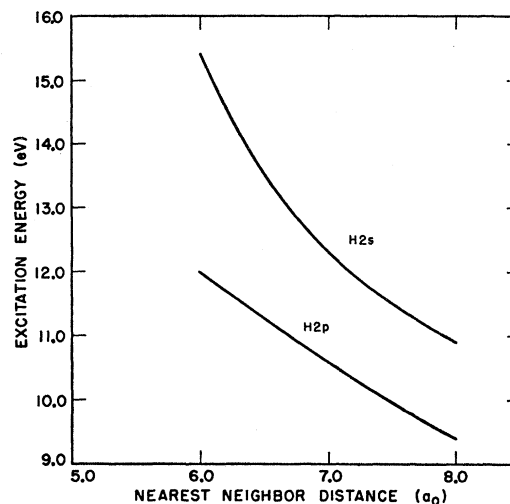
TABLE III. H  $2s$  excitation energy. Contributions to Ar:H  $1s-2s$  excitation energy as a function of nearest-neighbor distance. Numbers without explicitly quoted error are correct to the number of significant figures given.

Term	Nearest-neighbor distance ( $a_0$ )		
	6.0	7.0	8.0
$E_{at}$	51.8	26.8	17.7
$E_C$	-21.6	-8.2	-3.7
$E_X$	-19.3	-7.7	-3.6
$E_T$	$9.9 \pm 0.5$ eV	$3.8 \pm 0.2$ eV	$1.6 \pm 0.1$ eV
$E_{d-d}$	$-5.6 \pm 0.5$ eV	$2.2 \pm 0.2$ eV	$1.0 \pm 0.1$ eV
$E$	$15.4 \pm 1.0$ eV	$12.3 \pm 0.4$ eV	$10.9 \pm 0.2$ eV

<sup>10</sup> H. Kanzaki, Phys. Chem. Solids 2, 24 (1957).

and  $2s$  functions and the argon functions for a variety of interatomic distances. It also contains the values of  $N$  for the Ar:H system at 6.0, 7.0, and  $8.0a_0$  to emphasize the degree of nonorthogonality for the excited states. Figure 2 gives a plot of the H  $2p$ -Ar  $3s$  and H  $2p$ -Ar  $3p$  overlaps.

Table II details the results of the computation of the  $1s-2p$  energy at three nearest-neighbor distances. The errors quoted for each of the contributions of Eqs. (4)

FIG. 3. Hydrogen  $2s$  and  $2p$  excitation energies as a function of nearest-neighbor distance.

are computational errors arising from the expansions and numerical integration techniques employed. The van der Waals result is taken to give about 10% accuracy for the second-order terms. Table III gives the same information for the  $1s-2s$  energy difference. The contents of Tables II and III are summarized in Fig. 3, where the total excitation energies are plotted as a function of the nearest-neighbor distance. Table IV summarizes the results obtained for a nearest-

TABLE IV. Excitation energies and blue shifts for the nearest-neighbor distance of  $7.0a_0$ .

	Excited state	
	$2p$	$2s$
$E$	$10.6 \pm 0.2$ eV	$12.3 \pm 0.4$ eV
Shift	$0.4 \pm 0.2$ eV	$2.1 \pm 0.4$ eV

neighbor distance of  $7.0a_0$ . The shifts of the absorptions with respect to those of the free hydrogen atom, at 10.2 eV, are also included for reference. The value of  $10.6 \pm 0.2$  eV agrees closely with Baldini's<sup>5</sup> observed value of 10.56 eV for the first absorption in Ar:H. There is little doubt of the identification of this band as the hydrogen  $1s-2p$  transition, and hence the present tight-binding model seems clearly confirmed as an accurate quantitative picture of the absorption process.