An unusual observation was made when the high frequency was set within the ν_{31} absorption width, and the low frequency was driven through the ν_{21} resonance without stopping on a derivative maximum. With this procedure the low-frequency side of the ν_{21} resonance exhibited absorption, while emission occurred on the high-frequency side.

The object of further work will be to get information

about the $\Delta m = \pm 1$ and $\Delta m = \pm 2$ relaxation probabilities, using pulse techniques as well as steady-state resonance.[5,6] Because the nuclear magnetic quality factor is orders of magnitude larger than the Q for a circuit operating at a few Mc/sec, we do not expect maser operation with this spin system.[7]

[6] W. I. Goldberg, Bull. Am. Phys. Soc. 4, 251 (1959).
[7] J. Itoh, J. Phys. Soc. Japan 12, 1053 (1957).

Calculation of the g Factor of Hydrogen and the Alkali Atoms Trapped in Rare-Gas Solids

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The author's variational method of calculating g-factor shifts for atomic hydrogen trapped in a rare-gas solid is applied to the case of the alkali metals as impurities. An alternate derivation of the results is given and a simple physical model is discussed. The calculated shifts are compared with the experimentally observed ones for H, Li, Na, and K trapped in Ne, Ar, and Kr. Reasonable agreement is obtained if it is assumed that where two resonances have been reported the impurities are trapped at substitutional and octahedral interstitial lattice sites. The connection between the variational formalism and a previous perturbation treatment of Adrian is discussed and it is shown that a reinterpretation of the latter yields improved agreement with experiment. Crude estimates of the relaxation about substitutional and interstitial impurities are also given.

INTRODUCTION

THE experiments of Jen et al.[1,2] on the spin resonance of atomic hydrogen trapped in rare-gas solids at low temperature have led to the development of several explanations of the observed departure from free atomic hydrogen electron spin resonance spectra.[3,4] Recently, additional experimental results have become available for the paramagnetic resonance of the alkali metals trapped in rare-gas solids.[5,6] These provide a test of the theories and comparison with theory suggests what trapping sites are occupied in the experiments.

In this paper the author's variational method of calculating the g-factor shift is rederived for the alkali rare-gas systems by using Schmidt-orthonormalized

[1] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. 104, 846 (1956).
[2] S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, J. Chem. Phys. 32, 963 (1960).
[3] F. Adrian, J. Chem. Phys. 32, 972 (1960).
[4] D. Y. Smith, Phys. Rev. 131, 2056 (1963).
[5] C. K. Jen, V. A. Bowers, E. L. Cochran, and S. N. Foner, Phys. Rev. 126, 1749 (1962).
[6] J. P. Goldsborough and T. R. Koehler, Bull. Am. Phys. Soc. 7, 449 (1962).

wave functions to avoid the problems of convergence of the Löwdin overlap series.[4] Several physical models for picturing the mechanism by which the shifts occur are discussed in detail to supplement the formal development of Ref. 4. In addition, a comparison of the predictions of the variational calculation and perturbation theory calculations is made from several points of view.

Numerical values of the g-factor shifts are given for the variational calculation, the perturbation theory approach due to Adrian[3] and a modification of the perturbation formalism. It is found that the variational approach and the modified perturbation theory give reasonable agreement with experiment for the cases in which the impurity atom may be reasonably assigned to simple substitutional or interstitial sites.

THEORY

The problem of an impurity center in a rare-gas solid other than helium may be approached most reasonably from a static-lattice, tight-binding approximation. A zeroth-order approximation to the one-electron wave functions for such a system is given by the Hartree-Fock atomic functions. These, however, must be modified to take into account the spin-orbit, crystal field, and van der Waals interactions as well as wave function overlap in the crystal.

Using this model it has been shown that for atomic hydrogen as a dilute impurity, a shift in the hydrogen g factor from its free atomic value arises when the impurity's electronic wave function overlaps the states of rare-gas neighbors for which there is appreciable spin-orbit interaction. This treatment may be taken over to the case of the alkali metals as impurities provided the ground-state valence wave functions of the alkali atoms are not greatly distorted by the crystal environment.

That this condition holds may be inferred from the optical properties of the alkalies when trapped in the rare gases. In particular, the absorption spectrum of sodium in argon is only slightly changed from that of the free atom.[7] Aside from an increased number of lines arising from the lifting of degeneracies, the only change is a shifting of the lines that generally amounts to only a few percent and in no case is greater than ten percent. The major portion of these shifts presumably comes from perturbations of the excited states and it seems reasonable that the ground state is essentially atomic in character. It seems likely that this also holds for the other alkalies and rare gases.

The original variational calculation of spin resonance properties reported in Ref. 4 was made using Löwdin's method of symmetric orthogonalization.[8] There is, however, question about the convergence of the Löwdin series for the cases of large overlap.[8,9] We shall therefore present an alternate derivation using Schmidt orthogonalization.[10] The results are the same, but the method is simpler and physically clearer. As in previous work all terms up to the square of the overlap integrals will be retained.

Virtually all the g-factor shift arises from the effect of spin-orbit exchange terms between impurity and rare-gas p states. Roughly, this may be thought of as the result of the spin-orbit configuration interaction due to the electric field within the rare-gas atom acting on that part of the impurity wave function that overlaps the rare-gas atom. In addition to this effect, the corrections to the ground-state atomic functions due to the crystal field and van der Waals interactions mix in states of nonzero angular momentum which undergo a spin-orbit interaction in the field of the impurity nucleus. However, the last two effects may be shown to be negligible.

In particular, since the crystal field is localized "within" the rare-gas atoms, its effect will depend on the extent to which the impurity atom functions overlap those of the host. Calculations indicate that the g-factor shift arising from higher angular momentum states added by this field is proportional to the fourth power of the overlap integrals and, hence, is negligible in our approximation.

The g-factor shift due to the van der Waals interaction arises in the equivalent of fourth-order perturbation theory and may be shown to be approximately proportional to the van der Waals interaction times a matrix element of the spin-orbit interaction for the impurity divided by the square of an average energy denominator. In all cases considered in this work, the van der Waals interaction and the matrix elements of the spin-orbit interaction are small relative to the excitation energy so that the resulting g-factor shifts are less than one percent of the shifts due to the spin-orbit-overlap effect. However, this contribution could be important for impurities with large spin-orbit and van der Waals interactions but small overlaps with neighboring atoms.

The principal contribution to the g-factor shift arises from the spin-orbit and magnetic field interactions. We shall therefore consider the simplified crystal Hamiltonian[11]

$$\mathcal{3C} = \mathcal{3C}_0 + \mathcal{3C}_{so} + \mathcal{3C}_H, \tag{1}$$

where $\mathcal{3C}_0$ is the sum of free atomic Hamiltonians for the system,

$$\mathcal{3C}_{so} = -\frac{e\hbar}{4m^2c^2} \sum_i \boldsymbol{\sigma}_i \cdot \left[\mathbf{E} \times \left(\mathbf{p}_i - \frac{e}{c}\mathbf{A} \right) \right]$$

and

$$\mathcal{3C}_H = -\frac{e}{2mc} \sum_i (\mathbf{p}_i \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}_i) - g\frac{e\hbar}{4mc} \sum_i \boldsymbol{\sigma}_i \cdot \mathbf{H}.$$

Here $\mathbf{A}$ is the vector potential for the external magnetic field $\mathbf{H}$. $\mathbf{E}$ is the electric field within the crystal and e is the electronic charge (a negative number). $\boldsymbol{\sigma}$ is the Pauli spin operator in units of $\hbar/2$ and g is the electronic g factor. The symbols $\hbar$, m, c, and $\mathbf{p}$ have their usual meaning.

As has been discussed elsewhere,[4,12,13] the treatment of the vector potential and hence the angular momentum for a multicenter system in an external magnetic field must be made with care to avoid spurious terms arising from the change of origin from one center to another. It may be shown that the vector potential can be chosen arbitrarily for each group of matrix elements involving the same two centers if gauge-invariant wave functions are used.[4] In the rare-gas solids the interactions are, to a good approximation, between pairs of atoms, and we shall find it convenient to choose the origin of the vector potential as zero at the nucleus of the rare-gas atom for each of the rare-gas-impurity pairs.

To form the ground-state eigenfunctions of the crystal Hamiltonian we shall use an antisymmetrized product of orthonormalized one-electron wave functions. For

[7] M. McCarty and G. Robinson, Mol. Phys. 2, 415 (1959).
[8] P.-O. Löwdin, Advan. Phys. 5, 1 (1956).
[9] A. Gold, Phys. Rev. 124, 1740 (1961).
[10] See, for example, R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1953), Vol. I.

[11] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).
[12] C. P. Slichter, *Principles of Magnetic Resonances* (Harper and Row, Publishers, New York, 1963).
[13] F. London, J. Phys. Radium 8, 397 (1937).

these one-electron functions we choose the Hartree-Fock atomic functions and orthogonalize the impurity functions to the wave functions of the surrounding rare-gas atoms. Since the overlap drops off very rapidly with distance, only nearest neighbors will be considered.

Schmidt orthogonalization of the one-electron valence function of the alkali atom impurity $|\varphi^v)$ to the wave functions of the rare-gas $|\varphi^\alpha)$ gives

$$|\phi^v\rangle = (1 - \sum_\alpha S_{\alpha v}^2)^{-1}[|\varphi^v) - \sum_\alpha S_{\alpha v}|\varphi^\alpha)], \qquad (2)$$

where the angular bracket represents the orthogonalized function and the rounded brackets are used to denote atomic functions. The overlap integral $S_{\alpha\beta}$ is $(\varphi^\alpha|\varphi^\beta)$ and the sum over α runs over all the rare-gas atom wave functions.

Orthogonalization of the core functions of the alkalies to the rare-gas functions and the new valence functions $|\varphi^v)$ may be carried out by the same method, but contributions from these states are of order greater than S^2 so they are neglected.

For the present discussion, the important perturbation on the atomic Hartree-Fock functions is the spin-orbit interaction. At normal lattice spacings, it is easily shown that this is appreciable only near the rare-gas nuclei where the spin-orbit term in the Hamiltonian may be approximated by the atomic spin-orbit Hamiltonian. This is given by[11]

$$\mathcal{3C}_{so} = \sum_i \chi \mathbf{L}_{i,\xi} \cdot \boldsymbol{\sigma}_i$$

$$= \frac{e\hbar^2}{4m^2c^2} \sum_i \frac{1}{|\mathbf{r}_i - \mathbf{R}_\xi|} \frac{\partial V_\xi}{\partial |\mathbf{r}_i - \mathbf{R}_\xi|} \mathbf{L}_{i,\xi} \cdot \boldsymbol{\sigma}_i, \qquad (3)$$

where V_ξ is the intraatomic potential of the atom located at $\mathbf{R}_\xi$ and $\mathbf{L}_{i,\xi}$ is the angular momentum operator in units of $\hbar$ with $\mathbf{R}_\xi$ as origin for a coordinate $\mathbf{r}_i$.

To correct the Hartree-Fock wave functions for the configuration interaction, we modify the individual rare-gas functions and the rare-gas-like part of the orthogonalized impurity functions by the prescription[14]

$$|\varphi^\xi_{\text{corrected}}) = [1 + \mathcal{L}^\xi w^\xi (\mathbf{r} - \mathbf{R}_\xi) \mathbf{L}_\xi \cdot \boldsymbol{\sigma}]|\varphi^\xi_{\text{Hartree-Fock}}), \qquad (4)$$

where $\mathbf{R}_\xi$ is the position coordinate of the nucleus on which φ^ξ is centered, $\mathcal{L}^\xi$ is a parameter to be determined by the condition of minimum energy, and w^ξ is a function that corrects for the spin-orbit interaction.

It should be pointed out that in defining the corrected wave function by Eq. (4) we have not orthogonalized it to the occupied electronic states of the crystal. However, since it is used in the antisymmetrized product wave function for the crystal, the orthogonalization is automatically accomplished in the calculation. The terms representing this orthogonalization appear as the product of matrix elements subtracted from the leading terms in Eq. (5) for i_ξ' and $j_{\xi\xi}'$.

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[14] This method is a modification of a technique used by Hassé. See H. R. Hassé, Proc. Cambridge Phil. Soc. **26**, 542 (1930); and **27**, 66 (1931), also discussion in Ref. 4.

The coefficient of the spin-orbit term in the atomic Hamiltonian is spherically symmetric about the rare-gas nucleus. Hence, it is to be expected that any multiplicative correction to the wave function such as $\mathcal{L}^\xi w^\xi$ must also have the same symmetry. As discussed in Ref. 4 we shall choose for $\mathcal{L}^\xi w^\xi$ the simple function $\mathcal{L}^\xi|\mathbf{r} - \mathbf{R}_\xi|^{n'}$ where both $\mathcal{L}^\xi$ and n' are determined by minimization of the energy.

If the expectation value of the Hamiltonian, Eq. (1), for zero magnetic field is calculated to second power in the correction and then minimized we may solve for the spin-orbit parameter[4]

$$\mathcal{L}^\xi = -i_\xi'/j_{\xi\xi}', \qquad (5)$$

where

$$i_\xi' = (\mathcal{R}^\xi|\chi w^\xi|\mathcal{R}^\xi) - \sum_\eta (\mathcal{R}^\xi|w^\xi|\mathcal{R}^\eta)(\mathcal{R}^\eta|\chi|\mathcal{R}^\xi)$$

$$j_{\xi\xi}' = \tfrac{1}{2}(\mathcal{R}^\xi|(\partial w^\xi/\partial r + w^\xi/r)^2|\mathcal{R}^\xi)$$
$$- \sum_\eta (\mathcal{R}^\xi|w^\xi|\mathcal{R}^\eta)^2(\epsilon_\eta - \epsilon_\xi).$$

Here $\mathcal{R}^\xi$ is the radial part of φ^ξ and ϵ_ξ is its Hartree-Fock energy.

The magnetic energy levels for the system of an "s-state impurity" in a rare-gas crystal may be found by calculating the expectation value of the last term of the Hamiltonian using the crystal wave functions as corrected by the above process for the spin-orbit interaction. In particular, the g-shift tensor is given by the term linear in the spin-orbit parameter $\mathcal{L}^\xi$. From Eq. (6–1) of Ref. 4 this is

$$\mathbf{H} \cdot \Delta g \cdot \boldsymbol{\sigma} = 2 \sum_\xi \langle \phi^\xi | \mathcal{L}^\xi w^\xi (\boldsymbol{\sigma} \cdot \mathbf{LL} \cdot \mathbf{H} + \mathbf{H} \cdot \mathbf{LL} \cdot \boldsymbol{\sigma})|\phi^\xi\rangle$$
$$- \sum_\eta \langle \phi^\xi| \mathcal{L}^\xi w^\xi \boldsymbol{\sigma} \cdot \mathbf{L}|\phi^\eta\rangle\langle\phi^\eta|\mathbf{L} \cdot \mathbf{H}|\phi^\xi\rangle$$
$$- \sum_\eta \langle \phi^\xi| \mathbf{H} \cdot \mathbf{L}|\phi^\eta\rangle\langle\phi^\eta| \mathcal{L}^\xi w^\xi \mathbf{L} \cdot \boldsymbol{\sigma}|\phi^\xi\rangle. \qquad (6)$$

We have used the symbolic notation $\mathcal{L}^\xi w^\xi \mathbf{L}|\varphi^\xi\rangle$ to indicate that for $|\varphi^\xi\rangle = |\varphi^\xi\rangle + \sum_\alpha a_{\xi\alpha}|\varphi^\alpha\rangle$ (here normalization is neglected) we have

$$\mathcal{L}^\xi w^\xi \mathbf{L}|\phi^\xi\rangle = \mathcal{L}^\xi w^\xi \mathbf{L}_\xi|\varphi^\xi\rangle + \sum_\alpha a_{\xi\alpha}\mathcal{L}^\alpha w^\alpha \mathbf{L}_\alpha|\varphi^\alpha\rangle. \qquad (7)$$

That is, the index of $\mathcal{L}$, w, and $\mathbf{L}$ is just that of the wave function on which they operate. The operator $\mathcal{L}^\xi w^\xi \mathbf{L} \cdot \boldsymbol{\sigma}$ therefore projects out the correct excited state from each part of the wave function.

When the rare-gas wave functions and the orthogonalized impurity function are substituted in Eq. (6), it is found that the sum over closed shells of the rare gas and the impurity core leads to an identical cancellation of matrix elements involving only rare-gas states or core states. That is, in this model the rare-gas atoms behave as free atoms and have no paramagnetism. This also holds for the impurity core. However, matrix elements between rare-gas and impurity states do not sum to zero, but give a contribution of order S^2. The result is

$$\Delta g = -2(1 - \sum_\alpha S_{v\alpha}^2)^{-1} \sum_\alpha \mathcal{L}^\alpha$$
$$\times S_{\alpha v}[(\varphi^v|w^\alpha \Gamma|\varphi^\alpha) - \sum_\beta S_{v\beta}(\varphi^\beta|w^\alpha \Gamma|\varphi^\alpha)], \qquad (8)$$

where

$$\mathbf{\Gamma} = \hat{\imath}(L_iL_j + L_jL_i)\hat{\jmath}; \quad \hat{\imath},\hat{\jmath} = \hat{x},\hat{y},\hat{z}.$$

In deriving this the fact that φ^v is an s state has been used. Matrix elements such as $(\varphi^v|\mathbf{H}\cdot\mathbf{L}|\varphi^v)$ can then be evaluated by expanding φ^v in spherical harmonics about the rare-gas nucleus using the "α-function" technique.[8] This leads to a series expansion in which the terms have angular dependence Y_l^0 (for the z axis along the line joining the two nuclei), where Y_l^m is a normalized spherical harmonic. Then, regardless of the direction of $\mathbf{H}$, $(\varphi^v|\mathbf{H}\cdot\mathbf{L}|\varphi^v)$ is identically zero. Similarly terms such as $(\varphi^v|\mathbf{H}\cdot\mathbf{L}|\varphi^\eta)$ have been reduced to $S_{v\beta}(\varphi^\beta|\mathbf{H}\cdot\mathbf{L}|\varphi^\eta)$ by expanding φ^v in the complete set of rare-gas functions and using the fact that $\mathbf{H}\cdot\mathbf{L}$ does not connect φ^η to other than occupied states of the same shell.

To be consistent the term $\sum_\alpha S_{\alpha v}{}^2$ in the normalization correction should not be included since it represents an S^4 correction as may be seen by expanding the denominator. To order S^2 the isotropic g-factor shift is therefore

$$\Delta g = -4\sum_\alpha \mathcal{L}^\alpha S_{\alpha v}[(\varphi^v|w^\alpha L_z{}^2|\varphi^\alpha)$$
$$-\sum_\beta S_{v\beta}(\varphi^\beta|w^\alpha L_z{}^2|\varphi^\alpha)]. \quad (9)$$

Here the sum over α and β is restricted to occupied states β and α centered on the same atom. This is the same result as obtained with Löwdin's method of symmetric orthonormalization,[4] but here problems of convergence do not arise. The result holds for impurities with a single s-state valence electron outside a closed shell core provided $\sum_\alpha S_{\alpha v}{}^2$ is small compared to unity and the S^4 terms which have been neglected are indeed small.

A reasonable measure of the validity of the present approximation may be taken as the magnitude of $\sum_\alpha S_{\alpha v}{}^2$ relative to unity. For all the systems investigated, the impurity valence electron overlap with the outer p shell of the rare gas is less than 0.1 for substitutional impurities. The sum of overlaps should therefore be of the order of a tenth or less and the approximation should be good. For interstitial sites the overlaps are generally of the order of 0.1 to 0.15. For these the theory should also hold. In two interstitial cases—lithium and sodium in krypton—the overlap is greater than 0.15 and for these the theory is probably still valid, but near its limit of applicability.

Adrian has developed an alternate way of calculating the g shift using perturbation theory and the observed spin-orbit splitting of the outer p state in the rare gas.[3] This has been extended to the case of alkali atoms by Jen et al.[5] Their principle result is

$$\Delta g = (4/3E_L)\lambda_{p\sigma}S_{v,p\sigma}{}^2(\varphi^{p\sigma}|L_z{}^2|\varphi^{p\sigma}), \quad (10)$$

where E_L is the average excitation energy of the alkali atom and $\lambda_{p\sigma}$ is the spin-orbit splitting constant for the outer-most $p\sigma$ wave function $\varphi^{p\sigma}$ of the matrix rare-gas atoms. These authors also find a small correction

to this corresponding to the higher order terms due to overlap and the van der Waals interaction, but as we have shown, this is negligible in the S^2 approximation. A detailed comparison of the perturbation theory result with the variational approach will be given in the next two sections.

PHYSICAL PICTURE

A physical picture of the g-factor shift may be developed as follows. Consider the valence wave function of the impurity atom orthogonalized to the crystal matrix atoms by the Schmidt process. The interaction of the rare-gas atoms with the magnetic field is just their closed shell diamagnetism. However, the impurity interaction is that of an $^2S_{1/2}$ state modified by subtracting out the overlapping rare-gas wave functions.

In the neighborhood of the impurity nucleus the impurity's crystal wave function has an essentially free atom behavior and interacts with the magnetic field with a $g=2$ character. However, near the rare-gas atom the impurity wave function has a p-like part that undergoes a spin-orbit interaction. This part of the wave function interacts with magnetic field with a $g<2$ like character. The net result of the combination of these two interactions is to decrease the electronic g factor from its free atom value.
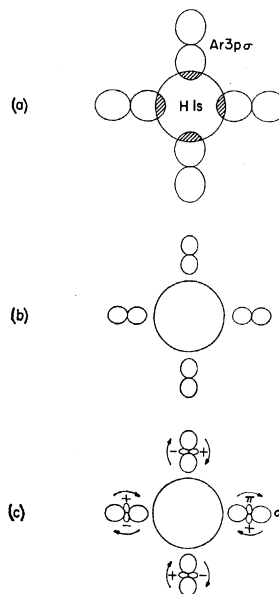

FIG. 1. A schematic representation of an s-state impurity overlapping the outer p shells of neighboring rare-gas atoms at an interstitial site. Part (a) shows the overlapping of the free atom s state of the impurity with the rare-gas α states. Part (b) shows the impurity function as Schmidt orthogonalized to the crystal atoms. Notice that the orthogonalized function still is mainly centered about the impurity, but that it has secondary centers at the neighboring atoms. Part (c) shows the admixture of excited π states to the impurity function by the spin-orbit configuration interaction. The arrows represent the resulting localized current loops. The signs on the lobes of the π states indicate the sign of the wave function in that lobe.
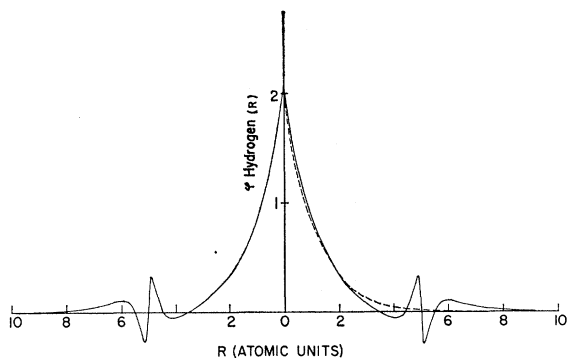
FIG. 2. The Schmidt orthonormalized wave function of hydrogen at an interstitial site in argon. The dashed curve shows the free atom hydrogen $1s$ state. The solid curve shows the $1s$ state as orthonormalized to the $3p$ states of the six nearest-neighbor argon atoms. This curve is drawn for a line passing through the nuclei of the impurity and two argon neighbors.

The wave function of the impurity may be visualized as in Fig. 1(a) and 1(b). In part (a) the impurity s-state wave function is drawn overlapping the $p\sigma$ states of its rare-gas neighbors. In (b) the orthogonalized impurity "crystal wave function" is shown. Here a portion of the rare-gas functions has been subtracted out causing a decrease in charge density of the free s state in the direction of the rare-gas atoms (shown as the "lumpiness" of the original spherical s state) and introducing some rare-gas p state centered on the neighboring sites.

This is shown quantitatively in Fig. 2 which gives a representative impurity wave function along a line joining two rare-gas atoms and passing through the impurity's nucleus. The dashed curve is the hydrogen $1s$ function for the free atom. The solid curve shows the hydrogen function as orthonormalized to the argon $3p$ states of six nearest neighbors of an octahedral trapping site.

Since the spin-orbit interaction has off-diagonal matrix elements between σ and π states, it mixes excited π states of the rare gas with the σ state part of the impurity function. This is indicated in Fig. 1(c) by the addition of π states to the impurity function.[15]

Individually both the σ state component from orthogonalization and the excited π states introduced by the spin-orbit interaction have quenched angular momentum, but their linear combination does not. It corre-

sponds to a localized current loop in the part of the impurity wave function near the rare-gas nuclei. The dipole moments of these spin-orbit-induced current loops are parallel to the direction of spin and consequently opposite to the spin magnetic moment. Since the total magnetic interaction is the sum of those of the spin moments and the atomic current loops, the interaction of the crystal with a magnetic field appears to be described by centers having electrons with a g factor reduced from the free atom value.

Another way of stating this is to say that the magnetic field interaction $\mathbf{L} \cdot \mathbf{H}$ couples the higher π states back to the impurity ground state. Since the radial parts of these higher π states are orthogonal to the occupied p states of the rare gas, the coupling is not to the rare-gas-like part of the ground state, but to the s-like hydrogen impurity state. In second-order perturbation theory this gives a term that decreases the interaction with the magnetic field.

Schematically this might be represented as in Fig. 3. Here the hydrogen impurity $1s$ state and the σ ground state of the rare gas are "connected" by overlap. The σ state is connected to the excited π states by the spin-orbit configuration interaction and the excited π state is connected back to the hydrogen ground state by overlap and the magnetic field interaction.

From a perturbation theory approach these connections can be seen easily. For simplicity we consider the spin-orbit correction to the rare-gas atom first and then orthogonalize the corrected rare-gas wave functions to the impurity. This is a legitimate procedure since the individual electrons in a closed shell undergo a spin-orbit interaction in the field of the rare-gas nuclei. However,

[15] It should be pointed out that the orthogonalized impurity function may be considered as a linear combination of eigenstates of a rare-gas atom since these states form a complete set. Of course, this sum for the impurity function does not contain any of the occupied rare-gas states and one would therefore say that the spin-orbit interaction is given by some complicated sum of spin-orbit interactions for the excited rare-gas states which are unknown. This is essentially true, but as can be seen from Fig. 2, in the immediate neighborhood of the rare-gas nucleus the impurity function is best described by a sum of the occupied states with coefficients given by the overlap integrals. This is obvious from Eq. (2) for the region where $|\varphi^v(\mathbf{r})| \approx 0$. Furthermore, since the spin-orbit interaction is determined only by the behavior of the impurity state near the neighbor nuclei, it will be the same as that for the occupied rare-gas states which are known.
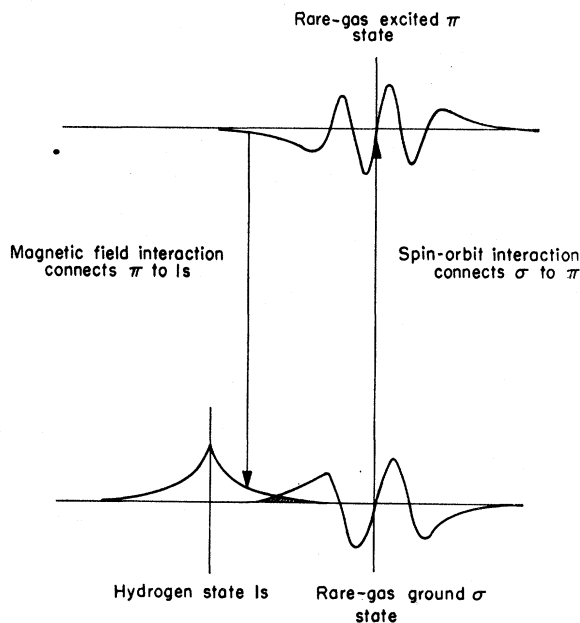

FIG. 3. The coupling of the impurity wave function to excited states of the crystal.

these individual interactions sum to zero for the shell as a whole leading to the somewhat misleading statement that there is no spin-orbit interaction for closed shells. In first-order perturbation theory the corrected rare-gas functions are

$$|\varphi^{\alpha\prime}\rangle = |\varphi^{\alpha}\rangle + \sum_{\gamma}{}' \, (\varphi^{\gamma}|\chi\mathbf{L}\cdot\boldsymbol{\sigma}|\varphi^{\alpha})(E_{\alpha}-E_{\gamma})^{-1}|\varphi^{\gamma}) , \quad (11)$$

where γ runs over all unoccupied rare-gas states and E_{α} is the energy of state φ^{α}.

Orthogonalizing this to the impurity ground state yields

$$|\phi^{v}\rangle = |\varphi^{v}\rangle - S_{\alpha v}[|\varphi^{\alpha}\rangle + \sum_{\gamma}{}' \, (\varphi^{\gamma}|\chi\mathbf{L}\cdot\boldsymbol{\sigma}|\varphi^{\alpha}) \\ \times (E_{\alpha}-E_{\gamma})^{-1}|\varphi^{\gamma})] . \quad (12)$$

The interaction of the impurity electron described by this wave function with a magnetic field gives matrix elements linear in $\boldsymbol{\sigma}$ and $\mathbf{H}$. They are

$$-2S_{\alpha v} \sum_{\gamma}{}' (\varphi^{v} - \sum_{\beta} S_{v\beta}\varphi^{\beta}|\mathbf{H}\cdot\mathbf{L}|\varphi^{\gamma}) \\ \times (\varphi^{\gamma}|\chi\mathbf{L}\cdot\boldsymbol{\sigma}|\varphi^{\alpha})(E_{\alpha}-E_{\gamma})^{-1} . \quad (13)$$

This can be simplified since $\mathbf{H}\cdot\mathbf{L}$ cannot connect the occupied rare-gas state φ^{β} to the excited rare-gas state φ^{γ}. Therefore the above reduces to

$$-2S_{\alpha v} \sum_{\gamma}{}' (\varphi^{v}|\mathbf{H}\cdot\mathbf{L}|\varphi^{\gamma}) \\ \times (\varphi^{\gamma}|\chi\mathbf{L}\cdot\boldsymbol{\sigma}|\varphi^{\alpha})(E_{\alpha}-E_{\gamma})^{-1} , \quad (14)$$

which explicitly shows the connection of the rare-gas excited state to the hydrogen atom ground state.

If the set of functions γ in Eq. (14) is completed by adding and subtracting matrix elements of occupied states and the usual sum rule arguments are made, we have after neglecting terms in $\varphi^{v}\chi$

$$\Delta g = 4 \sum_{\alpha,\beta} S_{v\alpha}S_{\beta v}(\varphi^{\alpha}|\chi L_{z}{}^{2}|\varphi^{\beta})\langle E_{\alpha}-E_{\gamma}\rangle_{\mathrm{av}}{}^{-1} , \quad (15)$$

where $\langle E_{\alpha}-E_{\gamma}\rangle_{\mathrm{av}}$ is the average excitation energy of the rare gas.

The problem may be viewed from a somewhat different angle by considering the excited states to which spin-orbit coupling occurs in an LCAO approximation. As a simple example consider the case of four rare-gas atoms at the corners of a square having the impurity at the center as in Fig. 1. Assuming, for simplicity, that there is only one localized rare-gas excited π state, $\psi(\mathbf{r})$, to which there is spin-orbit coupling, we may construct the four wave functions

$$\psi_{1} = \tfrac{1}{2}[\psi(\mathbf{r}-\mathbf{R}_{A}) + \psi(\mathbf{r}-\mathbf{R}_{B}) + \psi(\mathbf{r}-\mathbf{R}_{C}) + \psi(\mathbf{r}-\mathbf{R}_{D})] ,$$

$$\psi_{2} = \tfrac{1}{2}[\psi(\mathbf{r}-\mathbf{R}_{A}) + \psi(\mathbf{r}-\mathbf{R}_{B}) - \psi(\mathbf{r}-\mathbf{R}_{C}) - \psi(\mathbf{r}-\mathbf{R}_{D})] ,$$

$$\psi_{3} = \tfrac{1}{2}[\psi(\mathbf{r}-\mathbf{R}_{A}) - \psi(\mathbf{r}-\mathbf{R}_{B}) + \psi(\mathbf{r}-\mathbf{R}_{C}) - \psi(\mathbf{r}-\mathbf{R}_{D})] ,$$

$$\psi_{4} = \tfrac{1}{2}[\psi(\mathbf{r}-\mathbf{R}_{A}) - \psi(\mathbf{r}-\mathbf{R}_{B}) - \psi(\mathbf{r}-\mathbf{R}_{C}) + \psi(\mathbf{r}-\mathbf{R}_{D})] ,$$

from the localized states centered at $\mathbf{R}_{A}$, $\mathbf{R}_{B}$, $\mathbf{R}_{C}$, and $\mathbf{R}_{D}$, the position vectors of the rare-gas nuclei. If the spin-orbit mixing of these states into the ground state

is calculated for the field of each rare-gas atom and then summed over the four neighbors, it is easy to show that only the totally symmetric combination ψ_{1} leads to a net g shift.

It should be pointed out that the normalization factor of one-half does not lead to a correction of half the value given by our previous localized atomic orbital calculation. In detail this occurs because there is one spin-orbit term in the Hamiltonian for each of the four rare-gas atoms and because the relevant mixing elements are just half those for the localized atomic case.

As was pointed out in Ref. 4, a state made up of a totally symmetric combination of π states with no radial nodes centered on four symmetrically placed atoms about an impurity has the rotational properties of a g state. This may be seen either from Fig. 1(c) of this paper or from Fig. 2 in Ref. 4. In these the azimuthal nodal planes of the excited state lie both along lines to the rare-gas atoms and along the diagonals between the atoms. Since the excited states of the rare gases have radial functions with nodes, the LCAO excited state will have an even higher angular momentum character about the impurity. For example, assuming one radial node, one would expect to have at least an angular term with $L=8$, or k character.

In the case of hydrogen, the first g state occurs at $24/25$ of the ionization energy, and the first k state at $80/81$ of the ionization energy. Hence, in the picture in which just the impurity levels are considered, the spin-orbit interaction couples to very highly excited states, and, as was pointed out previously, the lowest possible energy for the energy denominator in Eq. (10) is substantially the ionization energy.[16]

It should be emphasized that the choice of orthogonalizing the impurity to the rare gas was arbitrary. The rare-gas wave functions could just as well have been orthogonalized to the impurity. In this case the impurity would have continued to act as a free atom, but the $p\sigma$ shells of the rare gas with spin parallel to the impurity would differ from those with spin antiparallel because the former overlap the impurity while the latter do not. No longer would the "circulation" caused by the spin-orbit interaction cancel for the electrons in the rare gas, but there would be a net moment opposite to that of the impurity centered on each of the neighboring atoms. The predictions of a calculation based on this model are the same as those for the model we have adopted.

In the Löwdin scheme, the orthogonalization is symmetric in the sense that each wave function is treated on an equal footing and each is modified by an "equal" amount. In this scheme the g shift can be thought of roughly as arising half from the impurity-orthogonalized-to-the-rare-gas scheme and half from the rare-gas-orthogonalized-to-the-impurity scheme.

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[16] The author is indebted to Professor C. P. Slichter for a discussion of this point.

COMPARISON OF PREDICTIONS

In the perturbation theory approach the choice of an energy denominator is not clearcut, though it certainly is some sort of average excitation for the spin-orbit interaction of the system of crystal plus impurity. As it has been shown, the excited states to which there is spin-orbit coupling are diffuse, and spread over a sphere of some two lattice spacings in diameter (14 or 15a_0 in the case of a substitutional impurity in argon). Because this type of function samples a great deal of the crystal, it is not obvious whether the energy of these states is determined primarily by the impurity or the rare-gas lattice.

In Adrian's work, in which attention was focused on the impurity, it seems appropriate to use an excitation energy of the impurity and, as we have argued from the LCAO picture, this cannot be significantly less than the ionization energy.

On the other hand, we may approach the problem by correcting the atomic rare-gas wave functions for the spin-orbit effect, and then form the crystal by bringing the impurity and the rare-gas atoms together. Orthogonalization mixes the corrected rare-gas states into the impurity function and the *g* factor is altered according to Eq. (15). In this case the corrections are given by the perturbation as calculated for the free rare-gas atom and the energy denominator appearing in the *g*-factor shift formula is given by the excitation energy of the rare gas. Clearly these are two equivalent approaches to the same problem. In the first, the functions are orthogonalized and then the spin-orbit interaction is taken into account, and in the second, the spin-orbit interaction is corrected for first and then the functions are orthogonalized. In principle, if the wave functions and energies were calculated exactly from either starting point, taking into account all perturbations, one would obtain a common solution. Presumably, that would be a band picture of the solid with impurity levels in the band gap.

For the systems considered here, the impurities will form deep-lying electron traps, and from the work of Koster and Slater,[17] the impurity levels may be thought of as being states localized about the impurity atom that have been split off the various energy bands of the pure crystal. Very little is known about impurities giving deep levels, but in the weak crystal environment of the rare gases it is reasonable to expect that the ground and first few excited states of the impurity would be relatively free atom-like. However, the highly excited states spread out in the rare-gas lattice, and their properties must be determined to a large degree by the rare gas in much the same way as the weakly bound donor states of impurities in semiconductors.[18]

The variational method as described here and in Ref. 4 starts by orthogonalizing the free atom Hartree-Fock functions and then making corrections for the spin-orbit interaction. It can be easily seen that the spin-orbit corrections could be made first and then the functions orthogonalized, and that in both instances the results are the same, namely, the *g*-factor shift is proportional to the spin-orbit parameter $\mathcal{L}$, multiplied by overlap matrix elements in the spin-orbit correction. The parameter $\mathcal{L}$ is determined to order S^0 by the rare-gas atom properties. However, as was shown in Ref. 4, the *g*-factor shift is given by a series in the variational parameters for the spin-orbit crystal field and van der Waal's interactions. To order S^2 only the spin-orbit term enters but if higher terms are retained, the other effects of the crystal environment are important.

In such a calculation, the spin-orbit parameter would also have to be found to a higher approximation. Without going into detail, one effect of this may be seen from the form of the denominator $j_{\xi\xi}$ of Eq. (5) for the spin-orbit parameter. The second term gives an S^2 contribution when exchange is included, and through this the details of the impurity can affect $j_{\xi\xi}$, which in effect is like an energy denominator. In particular this term tends to decrease the denominator if the impurity energy is less than that of the host and vice versa. In a sense, this is to be expected, since from the two possible perturbation theory pictures one would suspect the correct energy denominator lies between that of the impurity and that of the host. The variational approach further suggests that if a choice is to be made between the two proposed energy denominators, in the present approximation a preference should be given to using that of the rare gas.

RESULTS

The *g*-factor shifts for H, Li, Na, and K trapped in Ne, Ar, and Kr predicted by the variational calculation, Eq. (9), the perturbation theory treatment, Eq. (10), and the modified perturbation theory result, Eq. (15), are given in Table I. The experimental results of Jen *et al.*[5] are included for comparison.

The overlap integrals and matrix elements involved in this calculation were evaluated numerically on IBM-650 and -7070 computers at the University of Rochester's Computing Center using published Hartree-Fock atomic functions.[19] Graphical methods were used to minimize the spin-orbit energy with respect to n' and to interpolate between matrix elements evaluated for various values of the parameters. A list of the calculated spin-

[17] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); G. F. Koster, Phys. Rev. **95**, 1436 (1954); G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1959).

[18] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

[19] The following Hartree-Fock ground-state wave functions were used in evaluating the *g* shifts: Li—V. Fock and M. J. Petraschen, Physik. Z. Sowjetunion 8, 547 (1935); Na and K—L. Biermann and K. Lübeck, Z. Astrophys. **25**, 325 (1948); Ar—D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938); Kr—B. H. Worsley, Proc. Roy. Soc. (London) **A247**, 390 (1958); and R. E. Watson and A. S. Freeman, Phys. Rev. **124**, 1117 (1961); Ne—B. H. Worsley, Can. J. Phys. **36**, 289 (1958).

TABLE I. Experimental and theoretical values of the g-factor shift for hydrogen and the alkali metals as atomic impurities in the rare-gas solids.

| | Experiment | | | Predicted values of $-\Delta g \times 10^4$ | | | |
| | | | | Variation of calculation | | Perturbation theory | |
System	No. of resonances	$-\Delta g \times 10^4$	Site	No relaxation	Relaxed site	After Adrian	Modified
Ne:H	1	1.9	Sub.	0.23	0.25	0.25	0.29
			Oct.	1.1	0.77	1.7	1.9
Ar:H	2	0.60	Sub.	0.56	0.65	0.50	0.60
		6.5	Oct.	4.5	3.2	5.6	6.8
Kr:H	2	4.7	Sub.	2.0	2.3	2.0	2.4
		25.9	Oct.	18.0	14.0	26.0	31.0
Ne:Li	...	...	Sub.	1.1	0.99	5.0	1.8
			Oct.	0.94	0.92	5.4	1.9
Ar:Li	2	5.0	Sub.	5.0	5.3	22.0	8.2
		13.0	Oct.	7.4	6.6	39.0	15.0
Kr:Li	2	36.6	Sub.	22.0	24.0	110.0	39.0
		57.0	Oct.	35.0	30.0	220.0	82.0
Ne:Na	...	...	Sub.	1.1	0.92	5.0	1.8
			Oct.	0.80	0.80	4.4	1.6
Ar:Na	6	5.0	Sub.	5.2	4.6	23.0	8.6
		to 21.0	Oct.	6.7	6.1	36.0	13.0
Kr:Na	2	45.0	Sub.	23.0	22.0	120.0	42.0
		93.0	Oct.	32.0	29.0	210.0	76.0
Ne:K	...	...	Sub.	0.82	0.75	4.9	1.4
			Oct.	0.33	0.32	1.7	0.48
Ar:K	6	8.0	Sub.	5.2	4.6	31.0	9.3
		to 37.0	Oct.	3.4	3.7	25.0	7.4
Kr:K	2	59.0	Sub.	24.0	21.0	160.0	49.0
		174.0	Oct.	21.0	20.0	160.0	48.0

orbit parameters $\mathfrak{L}$ and the exponents n' for the rare gases are given in Table II. A reasonable estimate of the over-all accuracy of the numerical part of the calculations is probably $\pm 10\%$ exclusive of existing uncertainties in the published wave functions.

In evaluating the perturbation theory results, several approximations may be made in choosing values for the spin-orbit splitting λ and the average excitation energy. Adrian has taken λ to be approximately equal to the observed optical splitting for atoms having a missing p electron in an otherwise closed shell.[3] For example, for neon the splitting of fluorine is used. The first entry of Table III lists the values of λ for the rare gases in this approximation. The values are taken from the work of Barnes and Smith.[20]

λ may also be found by direct calculation from the

TABLE II. Variational parameters for the spin-orbit correction to rare-gas wave functions.

Rare gas and state	$\mathfrak{L}$ (atomic units)	n'
Neon—$2p$	3.89×10^{-4}	1.25
Argon—$3p$	1.50×10^{-3}	0.95
Krypton—$4p$	8.55×10^{-3}	0.75

Hartree-Fock wave functions and the self-consistent fields. The calculated values are given as the second entry of Table III. The matrix elements were evaluated by numerical integration using an interval of $0.05a_0$. Because of the rapid variations of the p-state wave functions and the self-consistent field near the nucleus of the rare-gas atom, the interval used may be too small in the immediate neighborhood of the nucleus. The effect of this would probably be to underestimate the spin-orbit splitting, but this is thought to lead to less than a 10% error.

TABLE III. The spin-orbit splitting of the outer p state of the rare gases in various approximations. Units are electron volts.

| | Spin-orbit splitting, λ | | |
Element	Spectra of next lower element	Calculated	Rare-gas spectrum
Neon	0.0501	0.0930	0.0963
Argon	0.109	0.152	0.175
Krypton	0.457	0.549	0.647
Xenon	0.943	...	1.13

An independent approximation for λ may also be obtained from the observed optical data on the rare gases. Knox[21] has made a Hartree-Fock calculation of

[20] R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 96 (1954).

[21] R. S. Knox, Phys. Rev. **110**, 375 (1958).

the 3*p* wave function for the excited argon configuration ($3p^5 4s$) and Gold and Knox[22] have calculated the 2*p* state for the excited neon configuration ($2p^5 3s$). In both cases it is found that the *p* function in the excited state is very little changed from that of the ground state. Consequently, the spin-orbit interaction should be approximately the same for both the ground and excited states. There is a small correction since the ground and excited states have a somewhat higher amplitude near the origin which increases the spin-orbit parameter, but at $0.05a_0$ this is only a 7% or 8% increase in amplitude for neon and 6% in argon so that the corrections would probably reduce the splitting by 10 or 15%.

Knox has fit the observed lines for the low-lying ($np^5 (n+1)s$) excited states of the rare gases with the theoretically expected formula and has derived the excited *p*-state splitting factor.[21] These are given as the third entry in Table III.

For all the rare gases listed, the parameter derived from the splitting of the "hole in a closed shell" approximation is less than the calculated value while the one derived from the optical transitions to the rare-gas excited states is greater. This is to be expected since the nuclear charge of the atom with one less electron is smaller and would probably lead to a smaller spin-orbit interaction. Furthermore, this should be a relatively smaller effect for heavier elements as is observed. On the other hand, for the excited states of the rare gas the *p* functions are larger near the nucleus than the ground-state functions are and the spin-orbit interaction derived from the spectra will be greater.

Table IV gives some relevant energies of the alkali

TABLE IV. Relevant energies for hydrogen, the alkalies, and the rare gases. The first excited states of the rare gases are metastable levels. Energies are given in electron volts.

Element	First excited state	Ionization energy	"Average" exc. pot.
H	10.2	13.6	11.9
Li	1.84	5.39	3.62
Na	2.10	5.14	3.62
K	1.61	4.34	2.98
Ne	16.6	21.6	19.1
Ar	11.6	15.8	13.7
Kr	9.91	14.0	12.0

atoms and the rare gases. The first excited state and the ionization energies are taken from the American Institute of Physics Handbook[23] and the average excitation energy has been calculated according to Adrian who has approximated it by the average of the energy of the first excited state and of the ionization energy.[3]

The *g*-factor shifts have been calculated using both the perturbation and the variational results for substitutional and interstitial sites in an undistorted lattice

and for the variational approach taking into account crude estimates of the effects of lattice relaxation[24] (see Appendix). In all the calculations, only the outer *p*-shell electrons of the rare gases have been considered.

In the case of perturbation theory two calculations are reported. In the first we follow Adrian and use the "average excitation energy" of the impurity and the hole in a closed shell approximation for the spin-orbit parameter.[25] The results are listed in the first column under "perturbation theory" in Table I. If the more appropriate ionization energy of the impurity is used as the energy denominator, the resulting *g*-factor shifts are reduced from the quoted ones by factors of 0.875 for hydrogen, 0.672 for lithium, 0.704 for sodium, and 0.686 for potassium.

In the second calculation the rare-gas average excitation potential and the calculated values of λ were used. The results are listed in the second column under "perturbation theory" in Table I. Hereafter, we shall refer to these as the "modified" perturbation theory results.

In six systems the experimental results show two distinct resonances. These are Ar:H, Kr:H, Ar:Li, Kr:Li, Kr:Na, and Kr:K. In the other cases, multiple resonances were either missing or more than two were observed. If both simple substitutional and interstitial trapping sites occur, they would be expected in the first four of these systems since the impurity atom is "smaller" than the rare-gas atoms. The last two cases are uncertain. Substitutional sites should exist, and since the impurity is not too much larger than the rare gas, the octahedral interstitial sites may be occupied. In the cases of "larger" impurities such as Ar:Na and Ar:K, substitutional sites probably exist, but simple interstitial trapping is much less likely.

A comparison of the experimental data shows that the higher *g*-factor shift values are associated with positive hyperfine shifts and the lower ones with a negative hyperfine shift. In the case of hydrogen, theory associates the negative hyperfine shift with a substitutional site and the positive one with the octahedral interstitial.[3,4] Carrying this assignment over to the alkali metals and assuming single atom impurities, a comparison of theory with experiment may be made. This is shown in Figs. 4 and 5.

In these figures the ratio of the predicted *g*-factor shift for a given site to the experimental value assigned to that site is given for the systems that showed two distinct resonances. If the results for interstitial Na and K in Kr are ignored, the variational calculation (circles) and the modified perturbation theory results (squares) are in better agreement with experiment than the unmodified perturbation results (triangles). The best agreement is generally given by the modified perturba-

[22] A. Gold and R. S. Knox, Phys. Rev. **113**, 834 (1959).
[23] *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1957).

[24] G. L. Hall, Phys. Chem. Solids **3**, 210 (1957).
[25] The values for hydrogen impurities differ from those reported by F. J. Adrian. Presumably this arises from differences in the calculation of the overlap integrals.

tion theory. This is to be expected since no extensive search for the best variational function has been made. A small improvement in the agreement of the variational results could be expected if the effects of inner shells and cross term contributions were included. On an average the modified perturbation theory results are somewhat greater than those observed, but this is reasonable because relaxation tends to decrease the shifts for cramped sites.

The results of both the variational calculation and the modified perturbation theory for the systems Kr:Na and Kr:K suggest that one of the resonances corresponds to a substitutional site, but that the other may be a trapping site of unknown geometry. While the unmodified perturbation theory gives reasonable agreement for the interstitial site, in the Kr:K system it fails for the substitutional one and so is unacceptable. Similarly, the agreement between the calculated results for a substitutional impurity and the lowest g shifts reported for Ar:Na and Ar:K suggest that in these systems substitutional sites are also occupied.

The sum of the squares of all the overlap integrals involved has been evaluated only for the argon-hydrogen system. For the substitutional site $\sum_\alpha S_{a v}{}^2$ is 0.0071 and for the interstitial site it is 0.091. Both values are small compared to unity justifying the assumptions made in the derivation of Eq. (9). Values of $\sum_\alpha S_{a v}{}^2$ for the other systems would presumably be of the same order of magnitude.

To see what effect relaxation of the lattice about the impurity would have on the g shift, results for the variational approach were calculated taking into account estimates of the relaxation. These are tabulated in Table I. Approximately the same percentage change would occur for all theories since the nearest-neighbor spacing enters only through the overlap integrals. In some cases there is improvement of the agreement with experiment, in others the agreement is worsened. However, the change due to the relaxation correction is
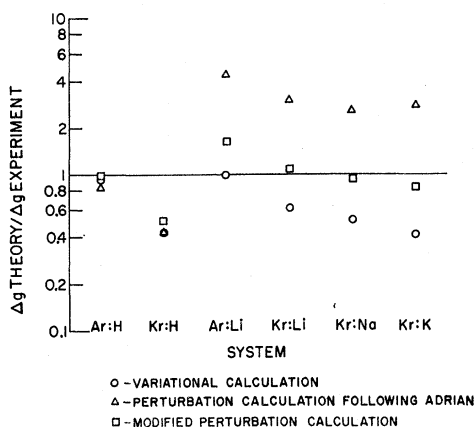

FIG. 4. The ratio of predicted to observed g-factor shifts for isolated impurity atoms in probable substitutional sites.
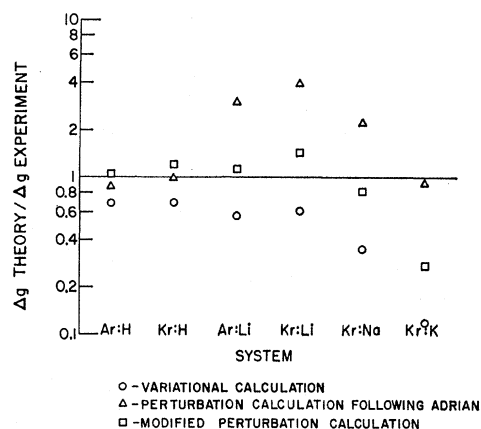

FIG. 5. The ratio of predicted to observed g-factor shifts for isolated impurity atoms in probable octahedral-interstitial sites.

generally less than 15% and probably is not significant considering the simplifications already introduced into the calculations.

CONCLUSIONS

The g shift for an impurity in a rare-gas solid appears to be given reasonably well by a variational treatment of the rare-gas spin-orbit splitting or a modification of the perturbation results of Adrian.

The present results have been obtained with a minimum of assumptions. Just the outer shell contributions have been considered and the simplest choice for the spin-orbit variational correction w^ξ has been made. A more realistic approach would be to use a polynomial for w^ξ and to include the effects of inner shells particularly for the heavier rare gases. This would be expected to increase the predicted g-shift values and generally would bring them into better agreement with experiment.

The good agreement between theory and experiment suggests that at low impurity concentrations simple substitutional sites are occupied in many cases of impurity trapping in the rare-gas solids and that octahedral-interstitial sites are present when "small" impurities are trapped. The trapping sites in systems where large numbers of resonances are observed probably include the substitutional, perhaps the interstitial, aggregates and vacancy-impurity combinations.

APPENDIX

To gain some insight into the nature of the trapping sites estimates of the relaxation about impurity atoms in rare gases were made. The substitutional site and the octahedral interstitial sites were considered and the calculations made by a modification of the techniques developed by Hall.[24]

To make these estimates it is necessary to know the form of the interaction between the rare gases and the impurity. We have taken this to be of the Lennard-Jones 6-12 form.[26] The coefficient of the R^{-6} term is just the van der Waals constant and is available from the work of Dalgarno and Kingston.[27] The coefficient of the repulsive part is harder to get at. It can be estimated by using the Lennard-Jones potential in the interaction-length-well-depth form.[28] From the semi-empirical rules developed from gas studies, the interaction length for a system is the sum of the interaction radii for the two atoms involved. These lengths are known for the rare gases.[29] However, for hydrogen and the alkali metals one must make a guess. For hydrogen the interaction length may be taken as the van der Waals radius quoted by Pauling.[30] For the alkali metals we have chosen half the internuclear distance in the metal solids.[31] This is reasonable since the rare-gas interaction radii are roughly half the internuclear distance in their solid phase. Furthermore, the Pauling-van der Waal radius is the equivalent distance in solid hydrogen.

Table V gives the results of the calculations. In the case of substitutional hydrogen in Ne, Ar, and Kr, and lithium in Ar and Kr, the relaxation is inward. In all other cases, both substitutional and interstitial, the relaxation is away from the impurity.

An analysis of Hall's theory indicates that the approximation for the interatomic potentials used is not accurate at displacements beyond 3 or 4% in which case the distortions are underestimated. Thus the larger values of relaxation should be taken only as order of magnitude estimates.

In the case of a 6-12 interatomic potential, a 5%

TABLE V. Relaxation of nearest neighbors about hydrogen and alkali atom impurities in rare-gas crystals. Given as percent of nearest-neighbor distance in the pure crystal.

System	Relaxation %	
	Substitutional	Octahedral interstitial
Ne:H	−1.03	+4.78
Ar:H	−1.34	+3.68
Kr:H	−1.27	+3.14
Ne:Li	+1.88	+5.18
Ar:Li	−1.19	+4.97
Kr:Li	−2.08	+4.86
Ne:Na	4.71	+5.33
Ar:Na	2.69	+5.23
Kr:Na	0.570	+5.10
Ne:K	6.37	+5.41
Ar:K	4.67	+5.29
Kr:K	3.55	+5.28

inward change of position from the minimum of the crystal energy leads to a change in energy of about 40%. This is to be compared with a change in energy of less than 10% for a 2% relaxation. Hence, we should expect that the larger displacements, if they exist at all, are severe distortions of the lattice energy wise and are probably not stable. On this basis we may reasonably expect to find simple substitutional and interstitial sites in systems where the displacements are small. This seems to be born out by the cases in which two separate resonances are observed.

Note added in proof. Since this work was completed, several experiments have been reported in detail. The studies of Goldsborough and Koehler[6,32] confirm the experiments of Jen et al.[5] but also show several new resonances of centers formed when the sample is exposed to thermal radiation during preparation. In all likelihood the latter centers do not represent isolated atoms trapped at simple sites, but are impurity complexes or vacancy-impurity combinations.

Experiments performed by Weyhmann[33] include an intensive study of the system of sodium in argon. The results also confirm the findings of Jen et al.,[5] but the studies have been extended to much lower alkali concentrations. It has been found that relatively narrow lines can be obtained at low concentrations and the sources of broadening have been investigated. As in the work of Goldsborough and Koehler[6,32] lines thought to arise from clusters of impurity atoms are also observed.

[26] J. E. Lennard-Jones, Physica 4, 941 (1937).
[27] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) 73, 455 (1959); and 78, 607 (1961).
[28] See, for example, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), pp. 22, 168.
[29] R. E. Dobbs and G. O. Jones, Rept. Progr. Phys. 20, 516 (1957).
[30] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), pp. 174, ff.
[31] See, for example, C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 40.

[32] J. P. Goldsborough and T. R. Koehler (to be published).
[33] W. Weyhmann and F. M. Pipkin, Bull. Am. Phys. Soc. 7, 84 (1962), and W. Weyhmann, Ph.D. thesis, Harvard University, 1963 (unpublished).