by the unitary transformation (independent of $\mathbf{k}$)[14]

$$\mathbf{t}=\frac{1}{\sqrt{2}}\begin{pmatrix} \mathbf{1} & \mathbf{i} \\ \mathbf{i} & \mathbf{1} \end{pmatrix}, \quad \text{for each } \mathbf{k}, \tag{A1}$$

where the submatrices of $\mathbf{t}$ are multiples of the unit matrix of order 3. Then, suppressing the index $\mathbf{k}$, if $\boldsymbol{\kappa}$ of (2.12) is written as $\boldsymbol{\kappa}_0+i\boldsymbol{\kappa}_1$, where $\boldsymbol{\kappa}_0$ and $\boldsymbol{\kappa}_1$ are real and symmetric,

$$\mathbf{d}=\mathbf{t}^{-1}\mathbf{a}\mathbf{t}=\begin{pmatrix} \boldsymbol{\gamma}-\boldsymbol{\kappa}_1 & \boldsymbol{\kappa}_0 \\ \boldsymbol{\kappa}_0 & \boldsymbol{\gamma}+\boldsymbol{\kappa}_1 \end{pmatrix}. \tag{A2}$$

$\mathbf{d}$ is easily inverted numerically to obtain $\boldsymbol{\mu}=\mathbf{d}^{-1}$. If $\boldsymbol{\mu}$ is represented in submatrix form as

$$\boldsymbol{\mu}=\begin{pmatrix} \boldsymbol{\mu}_1 & \boldsymbol{\mu}_2 \\ \boldsymbol{\mu}_3 & \boldsymbol{\mu}_4 \end{pmatrix}, \tag{A3}$$

then $\boldsymbol{\lambda}=\mathbf{t}\boldsymbol{\mu}\mathbf{t}^{-1}$ gives rise to the relations

$$\begin{aligned} \boldsymbol{\eta}&=\tfrac{1}{2}[(\boldsymbol{\mu}_1+\boldsymbol{\mu}_4)+i(\boldsymbol{\mu}_3-\boldsymbol{\mu}_2)], \\ \boldsymbol{\zeta}&=\tfrac{1}{2}[(\boldsymbol{\mu}_2+\boldsymbol{\mu}_3)+i(\boldsymbol{\mu}_4-\boldsymbol{\mu}_1)]. \end{aligned} \tag{A4}$$

These results are valid for any lattice with two atoms per unit cell for the case of central forces.

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[14] This transformation has been used by L. J. Slutsky and C. W. Garland, J. Chem. Phys. **26**, 787 (1957).

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Variational Theory of Paramagnetic Impurities in Van der Waals Crystals*†

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A consistent method of calculating the wave functions and electron-spin-resonance properties of a dilute paramagnetic impurty in a molecular crystal is outlined, and the system of atomic hydrogen in solid argon is treated as a detailed example. Starting from a one-electron, tight-binding, static-lattice picture of the impurity-doped crystal, the crystal wave function is formed as the antisymmetrized product of atomic Hartree-Fock functions. This is modified for the interactions in the crystal by adding variational corrections for crystal field effects, the spin-orbit interaction, and the Van der Waals interaction. The spin-resonance parameters are then found from the expectation value of the interaction with a magnetic field. The results lead to a reintepretation of parameters in previous theories and show that the various crystal perturbations do not add independently to give a net result when there is appreciable overlap between the impurity and host atoms. Estimates of the electronic g factor for hydrogen in argon are in good agreement with experiment. The predicted hyperfine shifts for substitutional hydrogen impurities also agrees well. However, it is shown that for interstitial sites the hyperfine-shift calculations are unreliable.

I. INTRODUCTION

RECENTLY both spin-resonance and optical-absorption spectra of isolated impurities trapped in rare-gas solids have been observed.[1–4] The outstanding feature of the results is that the spectrum of a dilute impurity is changed only slightly from the free-state spectrum by the crystal environment. Several theoretical treatments relating these shifts to the polarizability, spin-orbit splitting, etc., of the impurity and the host lattice have been given for specific systems. In these, additivity of the effects of the various crystal perturbations has been assumed and experimental data have been used to evaluate parameters in the models.[4,5]

The present work outlines a calculation of the ground-state wave function and electron-spin-resonance parameters of a tight-binding paramagnetic center in a rare-gas crystal. It is a "first principles" calculation in the sense that experimentally determined quantities are not used, and the major perturbations due to the crystal environment are calculated simultaneously so that effects depending on two or more interactions are retained. Specifically, the theory developed has been applied to the case of atomic hydrogen in argon, and order-of-magnitude estimates have been made as a guide for applying the theory in detail. Excited states and, therefore, optical properties could be treated, but more attention to overlap effects would be necessary.[6]

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[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] J. P. Goldsborough and T. R. Koehler, Bull. Am. Phys. Soc. **7**, 449 (1962).

[4] M. McCarty and G. Robinson, Mol. Phys. **2**, 415 (1959).

[5] F. Adrian, J. Chem. Phys. **32**, 972 (1960).

[6] For a review see D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 353. Examples of calculations include R. S. Knox, J. Phys. Chem. Solids **9**, 265 (1959); A. Gold, *ibid.* **18**, 218 (1961); Phys. Rev. **124**, 1740 (1961).

Starting from a one-electron, tight-binding, static-lattice picture of the impurity-doped crystal, the Pauli principle is satisfied by using an antisymmetric crystal wave function. This wave function is then modified by the addition of variational corrections of the correct symmetry to account for the perturbations on the tight-binding approximation due to the crystal field, spin-orbit interaction, and Van der Waals interaction.[7]

II. TRAPPING SITES IN RARE-GAS CRYSTALS

The rare gases crystallize in face-centered cubic lattices. For this study it is assumed that the impurity is in one of the three stable sites pointed out by Foner *et al.*,[2] namely, the substitutional site and two interstitial positions—an octahedral site at the center of the face-centered cube or a tetrahedral site near any corner of the face-centered cubic structure. The lattice may relax about the trapped atom, but the symmetry of the site is preserved because the ground electronic state is orbitally nondegenerate. Other possible trapping sites might be aggregates or vacancy-impurity combinations.

Preliminary calculations made in connection with this study indicate that in argon the nearest neighbors of a substitutional hydrogen atom relax by moving inward by about 1% of the equilibrium atomic separation for the pure crystal. This is reasonable since the hydrogen atom is "smaller" than the rare-gas atoms and would behave something like a vacancy for which the relaxation has been calculated to be 0.839% by Hall[8] and 0.32% by Kanzaki.[9] The additional relaxation inward arises from the long-range Van der Waal's attraction of the hydrogen not present in the case of the vacancy. For the octahedral position, the relaxation of the nearest neighbors is of the order of 4% outward. This is consistent with Hall's figure of 5% relaxation about an octahedral interstitial atom of the rare gas.

III. THE HAMILTONIAN

For a crystal consisting of N nuclei with charges $Z_J|e|\,(J=1,\cdots,N)$ and $\sum_J Z_J$ electrons, the Hamiltonian for electronic motion in the Born-Oppenheimer approximation is

$$\begin{aligned}\mathcal{H}=&-\frac{\hbar^2}{2m}\sum_i \nabla_i^2+e^2\sum_I\sum_{J>I}\frac{Z_IZ_J}{|\mathbf{R}_I-\mathbf{R}_J|}\\&+e^2\sum_i\sum_{j>i}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}-e^2\sum_i\sum_J\frac{Z_J}{|\mathbf{r}_i-\mathbf{R}_J|}\\&-\frac{e\hbar}{4m^2c^2}\sum_i\boldsymbol{\sigma}_i\cdot\left[\mathbf{E}\times\left(\mathbf{p}_i-\frac{e}{c}\mathbf{A}\right)\right]\\&-\frac{e}{2mc}\sum_i(\mathbf{p}_i\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p}_i)+\tfrac{1}{2}\beta_e g\sum_i\boldsymbol{\sigma}_i\cdot\mathbf{H}\\&+2\beta_e\beta_n\sum_i\sum_J\gamma_J\left\{\frac{(\mathbf{L}_i-\frac{1}{4}g\boldsymbol{\sigma}_i)\cdot\mathbf{I}_J}{|\mathbf{r}_i-\mathbf{R}_J|^3}\right.\\&+\frac{\frac{3}{4}g(\mathbf{r}_i-\mathbf{R}_J)\cdot\boldsymbol{\sigma}_i(\mathbf{r}_i-\mathbf{R}_J)\cdot\mathbf{I}_J}{|\mathbf{r}_i-\mathbf{R}_J|^5}\\&\left.+\tfrac{2}{3}\pi g\delta(\mathbf{r}_i-\mathbf{R}_J)\boldsymbol{\sigma}_i\cdot\mathbf{I}_J\right\}.\qquad(3.1)\end{aligned}$$

Here the symbols m, M, $\hbar$, and ∇ have their usual meaning. e is the electronic charge (a negative number) and $\mathbf{p}_i$ is the momentum operator $-i\hbar\nabla_i$. $\beta_e=|e|\hbar/2mc$, the Bohr magneton, and $\beta_n=|e|\hbar/2Mc$, the nuclear magneton. g is the electronic g factor, and γ is the nuclear g factor. $\mathbf{A}$ represents the vector potential for the external magnetic field, $\mathbf{H}$, and $\mathbf{E}$ is the electric field within the crystal. $\mathbf{I}_J$ is the spin operator in units of $\hbar$ for the Jth nucleus at position $\mathbf{R}_J$. $\boldsymbol{\sigma}_i$ is the Pauli spin operator in units of $\frac{1}{2}\hbar$ for the electron with coordinate $\mathbf{r}_i$, and $\mathbf{L}_i$ is the orbital angular-momentum operator in units of $\hbar$ for the same electron.

The first term in Eq. (3.1) is the kinetic energy of the electrons, the second, third, and fourth terms account for the electrostatic interaction of the electrons and nuclei,[10] and the fifth term is the spin-orbit interaction.[11] The sixth and seventh are the interaction with an external magnetic field, and the eighth is the hyperfine interaction of the electrons and nuclei.[12] The interaction of the electron with the magnetic field is taken only to first order in $\mathbf{H}$ since the quadratic terms are small for the fields involved and give rise to a diamagnetic effect which is not of interest in the present calculation.

In the case of hydrogen in a rare-gas crystal, the energy contributions fall into three groups:

I. The atomic binding energy (of order 10 eV or more).
II. The Van der Waals, crystal field, and spin-orbit energies (of order 0.1 to 0.001 eV or less).
III. The interaction with an external $\mathbf{H}$ field and the hyperfine interaction (of order 10^{-5} eV).

It follows from this division of the Hamiltonian that the interaction of the crystal with a magnetic field may be most reasonably found by starting with the Hartree-Fock wave functions for the free atoms, modifying

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[7] Since this work was begun a similar approach has been suggested in a discussion of transition ion complexes. See W. Marshall and R. Stuart, Phys. Rev. **123**, 2048 (1961).

[8] G. Hall, J. Phys. Chem. Solids **3**, 210 (1957).

[9] H. Kanzaki, J. Phys. Chem. Solids **2**, 24 (1957).

[10] See F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[11] For example see L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), 1st ed., p. 321; and E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1935), p. 130.

[12] For example, see L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (Pergamon Press, Inc., London, 1958), p. 486; and N. F. Ramsey in *Experimental Nuclear Physics*, edited by E. Segré, (John Wiley & Sons, Inc., New York, 1953), p. 381.

them for the interactions in group II, and using the results to find the expectation value of the interactions in group III.

The spin-orbit term and the orbital interaction with the magnetic field have been left in terms of the vector potential, to emphasize the importance of the choice of a convenient gauge. For a specific atom in the crystal, say, the Ith, we may choose the vector potential to be zero at the nucleus. Then to a good approximation for *this* atom, these interactions reduce to

$$+\frac{e\hbar^2}{4m^2c^2}\frac{1}{|\mathbf{r}-\mathbf{R}_I|}\frac{\partial V_I}{\partial(|\mathbf{r}-\mathbf{R}_I|)}\boldsymbol{\sigma}\cdot\mathbf{L}_I,$$

$$\text{and}\quad -\frac{e\hbar}{2mc}\mathbf{L}_I\cdot\mathbf{H},\qquad(3.2)$$

respectively. Here V_I is the intra-atomic potential of the Ith atom and L_I is the angular-momentum operator, with $\mathbf{R}_I$ as origin. However, for all other atoms in the crystal, the interactions are more complicated and involve the vector potential at the nucleus of the atom in question. This has been stressed by Slichter in his treatment of a paramagnetic center having a wave function made up of a linear combination of functions centered on two nuclei.[13]

In particular, for g-shift calculations, energy terms linear in $\mathbf{H}$ and $\boldsymbol{\sigma}$ are sought. In perturbation theory or an equivalent variational scheme, these arise in first order from the spin-orbit interaction because of the $\mathbf{A}\cdot\boldsymbol{\sigma}$ term and in second order from the cross product of the $\boldsymbol{\sigma}\cdot(\mathbf{E}\times\mathbf{p})$ and the $(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p})$ terms. Provided the vector potential is zero at the center on which the wave function being considered is located, the first-order term is negligible, and the second-order term reduces to the form $\mathbf{H}\cdot\mathbf{LL}\cdot\boldsymbol{\sigma}$, giving a g shift proportional to the tensor $\mathbf{LL}$. However, if $\mathbf{A}$ is nonzero, the first-order energy may be made arbitrarily large by the choice of gauge. This is offset by a corresponding change in the second-order term,[13] but both contributions must be considered.

To eliminate the problem of the arbitrariness of the gauge we shall use a method originated by London.[14] In this we introduce the gauge-invariant atomic wave functions defined by

$$\chi_\mu=\varphi_\mu\exp[(ie/\hbar c)\mathbf{A}_\mu\cdot\mathbf{r}],\qquad(3.3)$$

where $\mathbf{A}_\mu$ is the value of the vector potential at the nuclear position of the atomic wave function φ_μ. In calculating expectation values of the Hamiltonian, the differential operator in $\mathbf{p}$ "brings down" $\mathbf{A}_\mu$'s from the exponential, and these combine with the vector potential in the Hamiltonian to give operators depending on the vector potential as measured from the nucleus in question. The matrix elements of the Hamiltonian calculated using the χ's depend only on the difference in vector potential between the centers involved and are consequently gauge invariant.

In evaluating these matrix elements, the gauge may be chosen for convenience. For the problem at hand it is practical to take the origin of the vector potential at the rare-gas nucleus for each of the rare-gas-impurity pairs and to expand all other functions about these centers. This is a particularly useful choice for calculations of the g-factor shift since the spin-orbit interaction arises from the highly localized electric fields in the rare-gas atoms and hence lead to a Hamiltonian that is important only in the neighborhood of the rare-gas nuclei. Furthermore, because of this high degree of localization of the spin-orbit interaction, the contribution of each of the rare-gas atoms to the g-factor shift may be treated separately.

An effect noted by Bender[15] has been ignored. The hyperfine interaction leads to a slight difference in polarizability between hyperfine states. Consequently, the Van der Waals energy depends on the state, and an additional splitting is introduced. This could be included in the present formalism by adding a variational correction to account for the excited s states admixed to the impurity ground state by the hyperfine interaction. Only one-electron operators are involved and the theory would be formally the same as for the crystal field and spin-orbit corrections. For numerical estimates we shall use the perturbation theory results of Adrian[5] and Herman and Margenau.[16]

IV. THE CRYSTAL WAVE FUNCTION

To modify the wave function for the noninteracting atoms, a variational procedure similar to that of Hassé and Buckingham[17] is used, i.e., a correction is added to the wave function that is proportional to both the initial wave function and the perturbation. For example, if $\mathcal{H}_0$ is an unperturbed Hamiltonian having a ground-state eigenfunction ψ_0, and h is the perturbation; Hassé's method is to seek a solution of the form $\psi=(1+\lambda h)\psi_0$, where λ is a variational parameter.

In our case, the modified crystal wave function is taken to be

$$\Phi=\mathcal{A}[1+\textstyle\sum_\xi\mathcal{E}^\xi(\mathbf{r}_\xi)+\sum_\xi\mathcal{F}^\xi(\mathbf{r}_\xi)+\sum_{\xi,\eta}\mathcal{G}^{\xi\eta}(\mathbf{r}_\xi,\mathbf{r}_\eta)]\Phi_0,\qquad(4.1)$$

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[13] C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row Publishers, Inc., New York, 1963). The author is indebted to Professor Slichter for access to a prepublication manuscript of this text and for pointing out the importance of the vector-potential part of the spin-orbit interaction.

[14] F. London, J. Phys. Radium **8**, 397 (1937). The use of gauge-invariant wave functions here is equivalent to the unitary transformation, T, introduced by Adrian in a similar discussion of the electronic g factor of F centers, F. J. Adrian, Phys. Rev. **107**, 488 (1957).

[15] P. Bender, "Comments on Dr. Fontana's Paper" made at The Ann Arbor Conference on Optical Pumping, Ann Arbor, Michigan, 1959 (unpublished).

[16] R. Herman and H. Margenau, Phys. Rev. **122**, 1204 (1961).

[17] H. R. Hassé, Proc. Cambridge Phil. Soc. **26**, 542 (1930); **27**, 66 (1931); R. A. Buckingham, Proc. Roy. Soc. (London) **A160**, 94 and 113 (1937).

where $\mathcal{A}$ is the usual antisymmetrization operator $(N!)^{-1/2}\sum_{\nu=1}^{N!}(-1)^{P_\nu}P_\nu$ and Φ_0 is the product, $\prod_\xi\phi^\xi(\mathbf{r}_i)$, of the one-electron functions $\phi^\xi(\mathbf{r}_i)$, occupied by the N electrons of the system. In Eq. (4.1), the correction terms are

$$\mathcal{E}^\xi(\mathbf{r}_\xi)=\Lambda^\xi v^\xi(\mathbf{r}_\xi)\,,$$

$$\mathcal{F}^\xi(\mathbf{r}_\xi)=\mathfrak{L}^\xi w^\xi(\mathbf{r}_\xi)\mathbf{L}_\xi\cdot\boldsymbol{\sigma}_\xi\,,$$

and

$$\mathcal{G}^{\xi\eta}(\mathbf{r}_\xi,\mathbf{r}_\eta)=\lambda^{\xi\eta}u^{\xi\eta}(\mathbf{r}_\xi,\mathbf{r}_\eta)\,,$$

where Λ^ξ, $\mathfrak{L}^\xi$, and $\lambda^{\xi\eta}$ are variational parameters. The wave function $\phi^\xi(\mathbf{r}_\xi)$ is corrected by the function $v^\xi(\mathbf{r}_\xi)$ for crystal field effects, and by $w^\xi(\mathbf{r}_\xi)\mathbf{L}_\xi\cdot\boldsymbol{\sigma}_\xi$ for spin-orbit effects. The last term $u^{\xi\eta}(\mathbf{r}_\xi,\mathbf{r}_\eta)$ corrects the product of the wave functions ϕ^ξ and ϕ^η simultaneously for the Van der Waals or interatomic correlation effect.

If Hassé's method were to be extended literally, $v^\xi(\mathbf{r}_\xi)$ and $w^\xi(\mathbf{r}_\xi)\mathbf{L}_\xi\cdot\boldsymbol{\sigma}_\xi$ should be replaced by the crystal field potential, and the spin-orbit interaction, respectively. However, both are singular at the nuclei and lead to divergencies in the matrix elements. From the arguments of Shull and Löwdin[18] and the work of Wikner and Das,[19] it is expected that a solution can be obtained by using as our functions $v^\xi(\mathbf{r}_\xi)$ and $w^\xi(\mathbf{r}_\xi)$, a series $\sum_n c_n|\mathbf{r}_\xi-\mathbf{R}_\xi|^n$. For actual calculations only one term will be kept and a corrected wave function of the form

$$\phi\rightarrow(1+\lambda|\mathbf{r}_\xi-\mathbf{R}_\xi|^n)\phi\,, \tag{4.2}$$

where both λ and n are to be chosen to minimize the energy, will be used.

For $u^{\xi\eta}(\mathbf{r}_\xi,\mathbf{r}_\eta)$, the first term of the multipole expansion for the Van der Waals interaction will be used.[20] This is the familiar dipole-dipole term given by

$$\begin{aligned}u^{\xi\eta}(\mathbf{r}_\xi,\mathbf{r}_\eta)=e^2R^{-3}[&(\mathbf{r}_\xi-\mathbf{R}_\xi)\cdot(\mathbf{r}_\eta-\mathbf{R}_\eta)\\&-3(\mathbf{r}_\xi-\mathbf{R}_\xi)\cdot\hat{R}(\mathbf{r}_\eta-\mathbf{R}_\eta)\cdot\hat{R}].\end{aligned} \tag{4.3}$$

$\mathbf{R}_\xi$ and $\mathbf{R}_\eta$ are, respectively, the coordinates of the nuclei on which $\phi^\xi(\mathbf{r}_\xi)$ and $\phi^\eta(\mathbf{r}_\eta)$ are centered, $\mathbf{R}=\mathbf{R}_\xi-\mathbf{R}_\eta$ is the separation of the nuclei, $\hat{R}$ is the unit vector along $\mathbf{R}$, and $\mathbf{r}_\xi$ and $\mathbf{r}_\eta$ are the coordinates of the electrons. Here the discussion is limited to interatomic correlation by assuming $u^{\xi\eta}(\mathbf{r}_\xi,\mathbf{r}_\eta)=0$ if $\phi^\xi(\mathbf{r}_\xi)$ and $\phi^\eta(\mathbf{r}_\eta)$ are centered on the same nucleus.[21]

To simplify the calculations, Löwdin's method of symmetric orthonormalization[22] is applied to transform the atomic functions into the orthonormalized one-electron functions used to form Φ_0. For the particular unitary transformation introduced by Löwdin, the orthonormal functions ϕ^μ are given by the series

$$\phi^\mu=\varphi^\mu-\tfrac{1}{2}\sum_\alpha\varphi^\alpha S_{\alpha\mu}+\tfrac{3}{8}\sum_{\alpha,\beta}\varphi^\alpha S_{\alpha\beta}S_{\beta\mu}-\cdots\,, \tag{4.4}$$

where the φ^μ's are free atomic functions, and $S_{\alpha\beta}$ is the overlap between atomic wave functions φ^α and φ^β, $\int\varphi^{\alpha*}\varphi^\beta d^3r$.

This series converges if $\sum_\alpha|S_{\mu\alpha}|<1$. For the problem at hand, this convergence condition is satisfied for the substitutional site. For the octahedral and tetrahedral sites, it is satisfied if only outer shell overlaps are considered. If all shells are included, the question of convergence is not clear cut since this sufficiency condition is not met, but neither is a similar sufficient condition for divergence. However, for these "cramped" sites, there is a relaxation of the lattice outwards from the impurity, and so these cases would presumably be convergent also. For this study it is assumed that this series expansion is valid and that only terms up to order S^2 are important, i.e., the "S^2 approximation" is made. A more detailed discussion of convergence is given by Löwdin.[22]

Since our main concern is with the paramagnetic atom, not all the variational parameters will be equally important in calculating the magnetic effects. In particular, it is necessary to calculate $\lambda^{\xi\eta}$'s for all impurity-rare-gas interactions, but $\mathfrak{L}^\xi$ only for the rare gas, and Λ^ξ only for the impurity.

In calculating the Van der Waals parameters, matrix elements involving correlation corrections in two-, three- and four-electron coordinates are encountered. It is known that the three-electron term represents only 2 to 9% of the total cohesive energy,[23] so all but the two-electron term will be neglected.

The final assumption is that overlap integrals between host crystal atoms may be neglected. Their main role is to determine the repulsive forces between atoms, and thus the lattice structure for the pure crystal, which is taken as given. Since both the overlap and the Van der Waals interaction fall off rapidly with distance, it can be shown that the nearest neighbors of an impurity account for all but a few percent of the perturbations on the impurity. For numerical estimates, the "crystal" will, therefore, be defined as the impurity and its nearest neighbors.

V. CALCULATION OF THE VARIATIONAL PARAMETERS

A. The Crystal Energy

The variational parameters are found by minimizing the crystal energy ignoring the hyperfine and magnetic-field interactions. To avoid the complication of writing this energy in terms of atomic functions at this point, an abbreviated form for the matrix element is used. The wave function may be expanded as

$$\begin{aligned}\Phi=\mathcal{A}\Phi_0+\mathcal{A}\sum_\xi\mathcal{E}^\xi(\mathbf{r}_\xi)\Phi_0+\mathcal{A}\sum_\xi\mathcal{F}^\xi(\mathbf{r}_\xi)\Phi_0&\\+\mathcal{A}\sum_{\xi,\eta}\mathcal{G}^{\xi\eta}(\mathbf{r}_\xi,\mathbf{r}_\eta)\Phi_0&\,,\end{aligned} \tag{5.1}$$

$$=u_0+u_1+u_2+u_3\,,$$

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[18] H. Shull and P. O. Löwdin, J. Chem. Phys. **23**, 1362 (1955).

[19] E. G. Wikner and T. P. Das, Phys. Rev. **107**, 497 (1957).

[20] 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).

[21] For the separation of correlation energy into intra- and interatomic terms, see O. Sinanoğlu, J. Chem. Phys. **33**, 1212 (1960) and Phys. Rev. **122**, 493 (1961).

[22] P. O. Löwdin, Advan. Phys. **5**, 1 (1956).

[23] B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943); B. M. Axilrod, *ibid.* **19**, 719 and 724 (1951).

where u_0 is identified with $\mathfrak{A}\Phi_0$, u_1 with $\mathfrak{A}\sum_\xi \mathcal{E}^\xi(\mathbf{r}_\xi)\Phi_0$, etc.

In the tight-binding approximation, the correction to the normalization is very small compared to unity and may be expanded in a binomial series. Retaining terms up to the square of the variational parameters, this gives for the crystal energy,

$$\begin{aligned}E=\epsilon&+\{[\mu-\epsilon\alpha]_\Lambda+[(\nu-\epsilon\beta)-\alpha(\mu-\epsilon\alpha)]_{\Lambda^2}\}\\&+\{[M-\epsilon A]_{\mathfrak{L}}+[(N-\epsilon B)-A(M-\epsilon A)]_{\mathfrak{L}^2}\}\\&+\{[m-\epsilon a]_\lambda+[(n-\epsilon b)-a(m-\epsilon a)]_{\lambda^2}\}\\&+[P_{\Lambda\mathfrak{L}}-\epsilon C_{\Lambda\mathfrak{L}}-(\alpha M+A\mu)+2\epsilon\alpha A]_{\Lambda\mathfrak{L}}\\&+[P_{\Lambda\lambda}-\epsilon C_{\Lambda\lambda}-(\alpha m+a\mu)+2\epsilon\alpha a]_{\Lambda\lambda}\\&+[P_{\mathfrak{L}\lambda}-\epsilon C_{\mathfrak{L}\lambda}-(aM+Am)+2\epsilon aA]_{\mathfrak{L}\lambda},\end{aligned}\tag{5.2}$$

where, for $\mathcal{H}'$ the first-five terms of the Hamiltonian, Eq. (3.1), we have used the abbreviations

$$\begin{aligned}&\epsilon=\langle u_0|\mathcal{H}'|u_0\rangle,\\ \alpha&=2\langle u_1|u_0\rangle, &\mu&=\langle u_1|\mathcal{H}'|u_0\rangle+\langle u_0|\mathcal{H}'|u_1\rangle,\\ A&=2\langle u_2|u_0\rangle, &M&=\langle u_2|\mathcal{H}'|u_0\rangle+\langle u_0|\mathcal{H}'|u_2\rangle,\\ a&=2\langle u_3|u_0\rangle, &m&=\langle u_3|\mathcal{H}'|u_0\rangle+\langle u_0|\mathcal{H}'|u_3\rangle,\\ \beta&=\langle u_1|u_1\rangle, &\nu&=\langle u_1|\mathcal{H}'|u_1\rangle,\\ B&=\langle u_2|u_2\rangle, &N&=\langle u_2|\mathcal{H}'|u_2\rangle,\\ b&=\langle u_3|u_3\rangle, &n&=\langle u_3|\mathcal{H}'|u_3\rangle,\\ C_{\Lambda\mathfrak{L}}&=\langle u_1|u_2\rangle+\langle u_2|u_1\rangle, &P_{\Lambda\mathfrak{L}}&=\langle u_1|\mathcal{H}'|u_2\rangle+\langle u_2|\mathcal{H}'|u_1\rangle,\\ C_{\Lambda\lambda}&=\langle u_1|u_3\rangle+\langle u_3|u_1\rangle, &P_{\Lambda\lambda}&=\langle u_1|\mathcal{H}'|u_3\rangle+\langle u_3|\mathcal{H}'|u_1\rangle,\\ C_{\mathfrak{L}\lambda}&=\langle u_2|u_3\rangle+\langle u_3|u_2\rangle, &P_{\mathfrak{L}\lambda}&=\langle u_2|\mathcal{H}'|u_3\rangle+\langle u_3|\mathcal{H}'|u_2\rangle.\end{aligned}\tag{5.3}$$

The contributions of the first and second powers and the cross terms in the variational parameters have been grouped together in square brackets which are labeled with a subscript to indicate the term they contain. The energy in this approximation is a polynomial of second degree in the variational parameters. It may be written as

$$\begin{aligned}E=\epsilon&+\sum_\xi 2I_\xi\Lambda^\xi+\sum_\xi\sum_\eta J_{\xi\eta}\Lambda^\xi\Lambda^\eta\\&+\sum_\xi 2i_\xi\mathfrak{L}^\xi+\sum_\xi\sum_\eta j_{\xi\eta}\mathfrak{L}^\xi\mathfrak{L}^\eta\\&+\sum_\xi\sum_{\eta\neq\xi}2\Pi_{\xi\eta}\lambda^{\xi\eta}+\sum_\xi\sum_{\eta\neq\xi}\sum_\rho\sum_{\nu\neq\rho}\Upsilon_{\xi\eta,\rho\nu}\lambda^{\xi\eta}\lambda^{\rho\nu}\\&+\sum_\xi\sum_\eta 2K_{\xi\eta}\Lambda^\xi\mathfrak{L}^\eta+\sum_\xi\sum_\eta\sum_{\rho\neq\eta}2L_{\xi,\eta\rho}\Lambda^\xi\lambda^{\eta\rho}\\&+\sum_\xi\sum_\eta\sum_{\rho\neq\eta}2M_{\xi,\eta\rho}\mathfrak{L}^\xi\lambda^{\eta\rho}.\end{aligned}\tag{5.4}$$

The coefficients I_ξ, etc., are found by expanding the appropriate parts of Eq. (5.2) in terms of the Hamiltonian and the atomic wave functions. A skeletal outline of this procedure is given in the Appendix. Because of their length, more complete derivations are given elsewhere.[24]

Minimization of Eq. (5.4) leads to a set of coupled equations for the variational parameters. For Λ^ξ we find

$$\Lambda^\xi=\frac{I_\xi}{J_{\xi\xi}}-\frac{\sum_{\eta\neq\xi}\frac{1}{2}(J_{\xi\eta}+J_{\eta\xi})\Lambda^\eta+\sum_\eta K_{\xi\eta}\mathfrak{L}^\eta+\sum_\eta\sum_{\rho>\eta}L_{\xi,\eta\rho}(\lambda^{\eta\rho}+\lambda^{\rho\eta})}{J_{\xi\xi}}.\tag{5.5}$$

Similar expressions hold for the other parameters.

The leading terms, such as $I_\xi/J_{\xi\xi}$ in Eq. (5.5), arise directly from a perturbation on the free atom. On the other hand, the cross terms arise from considering an atom already corrected for one interaction being perturbed by a second. If the tight-binding approximation is valid, this "second generation" effect is of secondary importance compared to the leading terms and the equations can be solved by iteration. Furthermore, it is consistent to calculate the cross terms to order S^0 only, while calculating the leading terms to order S^2.

B. Crystal Field Parameters

Λ^ξ is given by Eq. (5.5) in terms of the energy equation coefficients I_ξ, $J_{\xi\eta}$, $K_{\xi\eta}$, and $L_{\xi\eta,\rho}$. These will be discussed for a hydrogen impurity atom. In atomic units I_ξ for $\xi=0$, the hydrogen $1s$ function, is given to second order in overlap by[25]

$$\begin{aligned}I_0=(0|v^0\bar{\Sigma}V_0|0)&-\sum_\eta(0|v^0|\eta)(\eta|\bar{\Sigma}V_0|0)\\&-\tfrac{1}{2}\sum_\alpha S_{0\alpha}\{(0|v^0\bar{\Sigma}V_\alpha|\alpha)+(\alpha|v^0\bar{\Sigma}V_0|0)\\&-(0|v^0|0)[(0|\bar{\Sigma}V_\alpha|\alpha)+2(\alpha|\bar{\Sigma}V_0|0)]\\&+[(0_i0_j|v_i^0r_{ij}^{-1}|0_i\alpha_j)-(0_i0_j|v_i^0r_{ij}^{-1}|\alpha_i0_j)]\},\end{aligned}\tag{5.6}$$

where the potential $\bar{\Sigma}V_\xi(\mathbf{r}_i)$ is shorthand for the "ex-

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[24] David Young Smith, Ph.D. thesis, University of Rochester, 1962 (unpublished). On file with University Microfilms, Ann Arbor, Michigan.

[25] Here we introduce the rounded-bracket notation

$$(\varphi^\xi|\text{Operator}|\varphi^\xi)$$

to indicate that the matrix elements are taken between atomic functions, φ^ξ's. Heretofore, we have used only matrix elements of Löwdin functions, ϕ^ξ's. These are indicated by the angular brackets $\langle\phi^\xi|\text{Operator}|\phi^\xi\rangle$. For simplicity of notation, we shall generally abbreviate wave functions with their quantum number index and indicate their associated coordinate by a subscript. Thus $(\varphi^\xi(\mathbf{r}_i)|$ will be denoted $(\xi_i|$.

change" potential defined by

$$\bar{\Sigma}V_\xi(\mathbf{r}_i)|\varphi_i{}^\xi) =-\sum_J{}'\frac{Z_J}{|\mathbf{r}_i-\mathbf{R}_J|}|\varphi_i{}^\xi)+\sum_{\eta\neq\xi}{}'(\eta_j|r_{ij}{}^{-1}|\eta_j)|\varphi_i{}^\xi) -(\eta_j|r_{ij}{}^{-1}|\xi_j)|\varphi_i{}^\eta). \quad (5.7)$$

Here the primes on the summations indicate that J does not include the atom on which φ^ξ is centered, and η does not include any function with the same center as φ^ξ.

The energy eigenvalues for the atomic wave functions have canceled, leaving matrix elements of potentials and the variational function v^ξ. Aside from exchange corrections, this has the general form of the matrix element of the crystal field times the variational correction less the product of the matrix elements of the crystal field and the variation.

In the case of a molecular crystal the electron on one atom will experience an attractive potential provided its wave function overlaps the intra-atomic potential of a neighboring atom. It is, therefore, to be expected that, if there is no overlap, I_ξ is zero and that I_ξ must have a leading term related to the electron overlap integrals. Actual calculations show that for hydrogen in argon the matrix elements of the potential, and hence I_ξ, are essentially proportional to the square of the hydrogen 1*s*-argon 3*p* overlap. The exchange corrections to the potential are also of order S^2 and arise from considering the interaction of the exchange charge clouds $\varphi^{\xi*}\varphi^\eta$ and $\varphi^{\eta*}\varphi^\xi$, where φ^ξ is a hydrogen function and φ^η a rare-gas function.

Since I_ξ is of order S^2, $J_{\xi\xi}$ is needed only to order S^0 to find Λ^0 to order S^2. The result in atomic units is

$$J_{\xi\xi}=\tfrac{1}{2}(\xi|\nabla v^\xi\cdot\nabla v^\xi|\xi). \quad (5.8)$$

This term arises from the kinetic-energy operator in Hamiltonian, and $J_{\xi\xi}$ may be considered as a measure of the kinetic energy added by the correction term $v^\xi\varphi^\xi$.

The second approximation to Λ^ξ is given by adding corrections in $J_{\xi\eta}$, $K_{\xi\eta}$, and $L_{\xi,\eta\rho}$. Since these cross terms are considered to order S^0 in finding Λ^ξ to order S^2, the term $\frac{1}{2}(J_{\xi\eta}+J_{\eta\xi})J_{\xi\xi}{}^{-1}\Lambda^\eta$ is negligible because Λ^η is of order S^2 in molecular crystals.

The cross term $K_{\xi\eta}J_{\xi\xi}{}^{-1}\mathfrak{L}^\eta$ is zero for the case of φ^ξ, a hydrogen 1*s* function. The main reason is that the coefficient $K_{\xi\eta}$ consists of overlap matrix elements involving the spin-orbit correction for a rare gas and an impurity state. These are of order S^2 and consequently negligible.

The cross term with the Van der Waals parameter $L_{\xi,\eta\rho}(\lambda^{\eta\rho}+\lambda^{\rho\eta})$, is given by

$$\begin{aligned}\sum_\eta\sum_{\rho>\eta}L_{\xi,\eta\rho}(\lambda^{\eta\rho}+\lambda^{\rho\eta}) &=\sum_{\rho\neq\xi}(\lambda^{\xi\rho}+\lambda^{\rho\xi})\{(\xi_i\rho_j|u_{ij}{}^{\xi\rho}v_{ij}v_i{}^\xi|\xi_i\rho_j)\\ &\quad-(\xi_i\rho_j|u_{ij}{}^{\xi\rho}v_{ij}|\xi_i\rho_j)(\xi|v^\xi|\xi)\}\\ &\quad-\sum_\eta\sum_{\rho>\eta}(\lambda^{\eta\rho}+\lambda^{\rho\eta})(\eta_i\rho_j|u_{ij}{}^{\eta\rho}v_{ij}|\eta_i\rho_j)(\xi|v^\xi|\xi), \quad (5.9)\end{aligned}$$

where v_{ij} is the dipole-dipole interaction between electrons with coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$, centered on two different atoms. For our choice of $u_{ij}{}^{\xi\rho}$, both v_{ij} and $u_{ij}{}^{\xi\rho}$ are the same and are given by Eq. (4.3).

The first half of this contribution arises from the interaction of $u_{ij}{}^{\xi\rho}$ and the normalized wave function as corrected for crystal field effects. The second term arises from the excess Van der Waals energy associated with the extent to which $(1+\Lambda^\xi v^\xi)\phi^\xi$ exceeds its normalized value.

C. Spin-Orbit Parameters

The solution of the variational calculation for the spin-orbit parameters is

$$\mathfrak{L}^\xi=\frac{i_\xi}{j_{\xi\xi}}-\frac{\sum_{\eta\neq\xi}\frac{1}{2}(j_{\xi\eta}+j_{\eta\xi})\mathfrak{L}^\eta+\sum_\eta K_{\eta\xi}\Lambda^\eta+\sum_\eta\sum_{\rho>\eta}M_{\xi,\eta\rho}(\lambda^{\eta\rho}+\lambda^{\rho\eta})}{j_{\xi\xi}}. \quad (5.10)$$

The spin-orbit parameters are important only for the *g*-shift calculations and always appear with coefficients proportional to S^2. Thus, $\mathfrak{L}^\xi$ is required only to order S^0.

For φ^ξ, a rare-gas wave function i_ξ is given by

$$i_\xi=(\xi|\chi w^\xi(\mathbf{L}\cdot\boldsymbol{\sigma})^2|\xi) -\sum_\eta(\xi|w^\xi\mathbf{L}\cdot\boldsymbol{\sigma}|\eta)(\eta|\chi\mathbf{L}\cdot\boldsymbol{\sigma}|\xi), \quad (5.11)$$

where χ is the spin-orbit factor $(\hbar^2/4m^2c^2)r^{-1}\partial V/\partial r$. Since only S^0 terms are considered; the sum on η runs over states centered on the same atom as φ^ξ.

This equation may be simplified by writing the wave functions as $\varphi^\xi=\mathfrak{R}^\xi(|\mathbf{r}|)y^\xi(\theta,\varphi)\delta(\xi)$, where $\mathfrak{R}^\xi(|\mathbf{r}|)$ is the radial part of φ^ξ, $y^\xi(\theta,\varphi)$ is its angular dependence, and $\delta(\xi)$ is its spin function. Then, since the spherical harmonics form a complete set for the angular-momentum operator, summing over closed shells in the second term leads to

$$i_\xi=\{(\mathfrak{R}^\xi|\chi w^\xi|\mathfrak{R}^\xi)-\sum_\eta(\mathfrak{R}^\xi|w^\xi|\mathfrak{R}^\eta)(\mathfrak{R}^\eta|\chi|\mathfrak{R}^\xi)\} \times(y^\xi\delta(\xi)|(\mathbf{L}\cdot\boldsymbol{\sigma})^2|y^\xi\delta(\xi)). \quad (5.12)$$

Here the sum over η runs over the non-*s* subshells.

The only appreciable terms in $j_{\xi\xi}$ are those arising from the kinetic-energy operator in the Hamiltonian. The equation for $j_{\xi\xi}$ may be reduced to simpler form as was i_ξ by using completeness for angular-spin operators. The result in atomic units is

$$j_{\xi\xi}=\{\tfrac{1}{2}(\mathcal{R}^\xi|[(\partial w^\xi/\partial r)+(w^\xi/r)]^2|\mathcal{R}^\xi)-\sum_\eta(\mathcal{R}^\xi|w^\xi|\mathcal{R}^\eta)^2(\epsilon_\eta-\epsilon_\xi)\}\times(y^\xi\delta(\xi)|(\mathbf{L}\cdot\boldsymbol{\sigma})^2|y^\xi\delta(\xi)), \tag{5.13}$$

where the sum over η runs over non-s subshells. Here the assumption that w^ξ is an s-like function has been used. For this choice,

$$\boldsymbol{\nabla}(w^\xi\mathbf{L}\cdot\boldsymbol{\sigma})=[(\partial w^\xi/\partial r)+(w^\xi/r)](\mathbf{L}\cdot\boldsymbol{\sigma})\hat{r}. \tag{5.14}$$

The cross term $\sum_{\eta\neq\xi}\frac{1}{2}(j_{\xi\eta}+j_{\eta\xi})\mathcal{L}^\eta j_{\xi\xi}^{-1}$ is found to be less than a thousandth of the leading term for $\mathcal{L}^\xi$, and may be neglected. The main reason for this is the small size of the function χ where the wave function is appreciable relative to the terms in $j_{\xi\xi}$ arising from the kinetic-energy operator. In addition, the cross term $K_{\eta,\xi}\Lambda^\eta/j_{\xi\xi}$ is of order S^2 for molecular crystals because it contains Λ^η and thus may be ignored.

The final cross term, $M_{\xi,\eta\rho}(\lambda^{\eta\rho}+\lambda^{\rho\eta})$, is similar to $L_{\xi,\eta\rho}(\lambda^{\eta\rho}+\lambda^{\rho\eta})$, but with $v^\xi(\mathbf{r}_j)$ replaced by $w^\xi(\mathbf{r}_j)\mathbf{L}_j\cdot\boldsymbol{\sigma}_j$.

D. Van der Waals Parameters

The solution of the variational calculation for the Van der Waals parameters shows that it is not possible to find a particular $\lambda^{\xi\eta}$, but that the system of equation can be solved for the sum $(\lambda^{\xi\eta}+\lambda^{\eta\xi})$. This is, of course, physically reasonable since we are calculating the Van der Waals interaction between two atoms and the effect, being a property of the system, cannot be divided between the atoms independently. Hence, in our case, the sum of the Van der Waals parameters $\lambda^{\xi\eta}$ and $\lambda^{\eta\xi}$ has meaning, but separated, the individual terms do not.

The Van der Waals parameter for minimum energy is given by

$$\lambda^{\xi\eta}+\lambda^{\eta\xi}=\frac{\Pi_{\xi\eta}}{\Upsilon_{\xi\eta,\xi\eta}}-\frac{\sum_\rho\sum_{\nu>\rho}{}_{\rho\nu\neq\xi\eta}\frac{1}{2}(\Upsilon_{\xi\eta,\rho\nu}+\Upsilon_{\rho\nu,\xi\eta})(\lambda^{\rho\nu}+\lambda^{\nu\rho})+\sum_\rho L_{\rho,\xi\eta}\Lambda^\rho+\sum_\rho M_{\rho,\xi\eta}\mathcal{L}^\rho}{\Upsilon_{\xi\eta,\xi\eta}}. \tag{5.15}$$

$(\lambda^{\xi\eta}+\lambda^{\eta\xi})$ has a leading term proportional to S^0, that is, overlap is not essential for the Van der Waals interaction. The S^2 terms are extremely complicated and give little understanding of the processes at work. Hence, only the direct terms will be presented here.

Neglecting overlap, the term $\Pi_{\xi\eta}$ is given to order S^0 by

$$\Pi_{\xi\eta}=(\xi_i n_j|u_{ij}^{\xi\eta}r_{ij}^{-1}|\xi_i\eta_j). \tag{5.16}$$

This term represents the electrostatic interaction between the electrons in states φ_i^ξ and φ_j^η as modified by $u_{ij}^{\xi\eta}$. It can be put in a more familiar form by adding the quantity

$$(\xi_i\eta_j|u_{ij}^{\xi\eta}(|\mathbf{R}_I-\mathbf{R}_J|^{-1}-|\mathbf{r}_i-\mathbf{R}_J|^{-1}-|\mathbf{r}_j-\mathbf{R}_I|^{-1})|\xi_i\eta_j),$$

which is zero by the oddness of $u_{ij}^{\xi\eta}$. The result is explicitly the matrix element of the interaction of two neutral charge clouds. This interaction may be expanded in a multipole series and the usual expression for Van der Waals interactions results.

The term $\Upsilon_{\xi\eta,\xi\eta}$ is given by the matrix elements arising from the kinetic energy operators in the Hamiltonian. To order S^0 it is

$$\Upsilon_{\xi\eta,\xi\eta}=\tfrac{1}{2}(\xi_i\eta_j|\boldsymbol{\nabla}_i u_{ij}^{\xi\eta}\cdot\boldsymbol{\nabla}_i u_{ij}^{\xi\eta}+\boldsymbol{\nabla}_j u_{ij}^{\xi\eta}\cdot\boldsymbol{\nabla}_j u_{ij}^{\xi\eta}|\xi_i\eta_j). \tag{5.17}$$

No cross terms involving $\Upsilon_{\xi\eta,\rho\nu}$ appear since these are of order S^2, the S^0 terms vanishing because of the oddness of $u_{ij}^{\xi\eta}$. This also holds for the cross terms $L_{\rho,\xi\eta}\Lambda^\rho$ since, as we have shown, Λ^ρ is of order greater than S^0. While the cross term involving the spin-orbit interaction is of order S^0, it is found to be negligible compared to the leading Van der Waals terms. This can easily be seen since both Eqs. (5.16) for $\Pi_{\xi\eta}$, and (5.17) for $\Upsilon_{\xi\eta,\xi\eta}$ are roughly either sums or products of dipole matrix elements for the charge distributions $|\varphi^\xi|^2$ and $|\varphi^\eta|^2$. For the ground state, these are of order unity. However, the spin-orbit correction may be shown to lead to matrix elements of order 10^{-3} or so.

VI. CALCULATION OF ELECTRON SPIN RESONANCE PARAMETERS

A. The Hyperfine and Magnetic Field Perturbations

The magnetic energy levels for a ${}^2S_{1/2}$ state are obtained from the Breit-Rabi formula,[26] which gives the energy levels in terms of the magnetic field and two parameters: The hyperfine splitting in the absence of a magnetic field, A, and the electronic g factor.

The g factor is a measure of the interaction of the spin of the electron with the magnetic field and in general is a dyadic. Since the experiments on impurities in rare gases are generally done with polycrystalline samples, only the isotropic part is considered. It is the coefficient of $\frac{1}{2}\beta_e\mathbf{H}\cdot\boldsymbol{\sigma}$ in the interaction of the solid with the magnetic field. This interaction arises from the sixth and seventh terms in the Hamiltonian, Eq. (3.1). The hyperfine interaction is given by the last term in the Hamiltonian. For the present problem, only the Fermi contact interaction is important.

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[26] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2083 (1931).

These terms in the Hamiltonian are all sums of one-electron operators, and their expectation values may be written down in analogy with the terms in the expression for the crystal energy, Eq. (5.2). The result is a polynomial in the variational parameters. We shall use the same symbols for the coefficients in this polynomial as we did in Eq. (5.4), but with primes added to distinguish them from the crystal-energy terms.

B. The *g* Shift

For an impurity with an *s* electron having unpaired spin, the *g* shift arises almost exclusively from the spin-orbit interaction correction to the rare-gas wave functions and the fact that in the solid the wave functions of the impurity overlap the rare-gas atoms. A *g* shift corresponding to higher angular-momentum states admixed to the impurity ground state by the crystal field and the Van der Waals interactions exists, but is negligible compared to the spin-orbit overlap effect.

The constant term in the energy polynomial for the magnetic field interaction, ϵ', includes a sum over all electronic states. The contributions of the closed-shell rare-gas states sum to zero, leaving only the impurity term which is identical to the interaction of the free impurity with the magnetic field.

The Λ, λ, λ^2, and $\Lambda\lambda$ contributions consist of terms of the form $\langle\nu|Qh_H|\nu\rangle-\langle\nu|Q|\nu\rangle\langle\nu|h_H|\nu\rangle$ or sums of terms multiplied by $\langle\nu|h_H|\eta\rangle$, $\eta\neq\nu$, where Q is an arbitrary operator and h_H, the magnetic field interaction, is the sixth plus seventh terms of the Hamiltonian. Since Löwdin functions are spin eigenfunctions, these terms cancel identically or are zero by orthogonality.

The *g* shift arises from the term linear in the spin-orbit parameter, $\mathfrak{L}^\xi$, which is

$$\begin{aligned}M'-\epsilon'A=\textstyle\sum_\xi \mathfrak{L}^\xi[&\langle\xi|w^\xi\mathbf{L}\cdot\boldsymbol{\sigma}h_H+h_Hw^\xi\mathbf{L}\cdot\boldsymbol{\sigma}|\xi\rangle\\ &-\textstyle\sum_\eta\langle\xi|w^\xi\mathbf{L}\cdot\boldsymbol{\sigma}|\eta\rangle\langle\eta|h_H|\xi\rangle\\ &-\textstyle\sum_\eta\langle\xi|h_H|\eta\rangle\langle\eta|w^\xi\mathbf{L}\cdot\boldsymbol{\sigma}|\xi\rangle].\end{aligned}\tag{6.1}$$

Expanding the operator in the first term, we have for w^ξ an *s*-like function

$$w^\xi\mathbf{L}\cdot\boldsymbol{\sigma}h_H+h_Hw^\xi\mathbf{L}\cdot\boldsymbol{\sigma}=\beta w^\xi(\boldsymbol{\sigma}\cdot\boldsymbol{\Gamma}\cdot\mathbf{H}+g\mathbf{L}\cdot\mathbf{H}),\tag{6.2}$$

where $\boldsymbol{\Gamma}=\hat{\imath}(\mathbf{L}_i\mathbf{L}_j+\mathbf{L}_j\mathbf{L}_i)\hat{\jmath}$; $i, j=x, y, z$. $\boldsymbol{\Gamma}$ is the operator corresponding to the *g*-shift tensor.

Considering just those parts of Eq. (6.1) involving $\boldsymbol{\Gamma}$, it is found on expansion to order S^2, that the second two terms of Eq. (6.1) are cancelled in order S^0 by the first term. This happens because the sum over η runs over a set that is complete for the angular operators. A term of order S^2 remains, however. The result of simplifying this is

$$\begin{aligned}\Delta\mathbf{g}=-2\textstyle\sum_\alpha \mathfrak{L}^\alpha S_{\alpha0}&\\ \times[(0|w^\alpha\boldsymbol{\Gamma}|\alpha)&-\textstyle\sum_\beta S_{\beta0}(\beta|w^\alpha\boldsymbol{\Gamma}|\alpha)],\end{aligned}\tag{6.3}$$

where α and β are rare-gas p states centered on the same atom.

All contributions involving $\mathfrak{L}^2$, $\mathfrak{L}\Lambda$, and $\mathfrak{L}\lambda$ may be treated in a similar manner, but because of the cancellation of S^0 terms, no contribution results.

The shifts due to higher angular-momentum states introduced to the ground state of the impurity by the crystal field and Van der Waals interactions, do not arise directly from the variational calculation, but come about naturally when the wave functions resulting from the calculation are considered as the correct starting functions for a perturbation calculation of the spin-orbit and magnetic field interactions. These *g* shifts occur in the second-order energy term and are proportional to the square of the variational parameters associated with the higher angular-momentum states. In the case of the crystal field, this leads to a change in *g* of order S^4 which is negligible in the present approximation. The shift due to the Van der Waals interaction is not obviously negligible. However, numerical calculations show that its contribution is less than 1% of the observed shifts in the reported hydrogen-rare-gas systems and even less for the alkali metal-rare-gas systems.

C. The Hyperfine Splitting

The shift in hyperfine splitting arises from renormalization associated with orthogonalization of the one-electron wave functions and both the crystal field and the Van der Waals corrections. The spin-orbit interaction makes no contribution to the splitting.

The renormalizing effect appears in the constant term and leads to the expression

$$\frac{\Delta A_{\text{overlap}}}{A}=\sum_\alpha S_{0\alpha}{}^2-2\sum_\mu S_{\mu0}\frac{(0|\delta(\mathbf{r}-\mathbf{R}_0)|\mu)}{(0|\delta(\mathbf{r}-\mathbf{R}_0)|0)},\tag{6.4}$$

where A is the hyperfine splitting for atomic hydrogen.

The contribution of the crystal field interaction appears as a normalization correction to the density of the hydrogen atom's wave function. The result is

$$\Delta A_{\text{crystal field}}/A=-2\Lambda^0(0|v^0|0).\tag{6.5}$$

The Van der Waals correction makes two contributions. The first is proportional to λ and appears in order S^2 since all $S^0\lambda$ contributions integrate to zero because of the oddness of $u_{ij}{}^{\xi\eta}$. The result is given by

$$\begin{aligned}\frac{\Delta A_{\text{vdW}(\lambda)}}{A}&\\ =-2\sum_{0<\eta}(\lambda^{0\eta}+\lambda^{\eta0})&\Bigg\{\frac{(0_i\eta_j|u_{ij}{}^{0\eta}\delta(\mathbf{r}_j-\mathbf{R}_0)|\eta_i0_j)}{(0|\delta(\mathbf{r}-\mathbf{R}_0)|0)}\\ &-(0_i\eta_j|u_{ij}{}^{0\eta}|\eta_i0_j)+\sum_{\alpha\neq\eta}{}^{\eta}S_{\alpha0}(0_i\eta_j|u_{ij}{}^{0\eta}|\eta_i\alpha_j)\Bigg\},\end{aligned}\tag{6.6}$$

where the symbol $\sum^\eta{}_{\alpha\neq\eta}$ indicates the sum over α where φ^α and φ^η are on the same atom, but are not the same state. The second contribution is proportional to

λ^2 and again represents a normalization correction. It is

$$\Delta A_{\mathrm{VdW}(\lambda^2)}/A = -\sum_{0<\eta} (\lambda^{0\eta}+\lambda^{\eta 0})^2 (0_i\eta_j|\,(u_{ij}{}^{0\eta})^2|0_i\eta_j)\,. \quad (6.7)$$

The $\Lambda\mathfrak{L}$, $\mathfrak{L}\lambda$, and $\Lambda\lambda$ cross terms do not contribute since the λ terms are zero to order S^0 because of the oddness of $u_{ij}{}^{\xi\eta}$, and the Λ terms vanish to order S^0 since Λ itself is of order S^2.

VII. ORDER OF MAGNITUDE CALCULATIONS AND DISCUSSION

As a sample of the calculations involved, the leading terms in the solutions for the variational parameters have been evaluated and from these the hyperfine splitting and the g shift have been predicted for a hydrogen atom trapped in the substitutional and the octahedral sites of an argon lattice.[27]

A. The Variational Parameters

The variational parameters for hydrogen as an impurity in argon were evaluated through terms in intra-atomic exchange. Interatomic exchange was neglected for the approximate calculation of these parameters. The results are shown in Table I.

TABLE I. Calculated variational parameters for the argon-hydrogen system.

Variational function	Parameter values in atomic units
Crystal field—variational form $\Lambda^{\eta}r^n$ (representative value at $R=6.5a_0$ for $\eta=$hydrogen 1s state)	$\Lambda^0=1.65\times10^{-5}$ $n=4.5$
Spin orbit—variational form $\mathfrak{L}^{\eta}r^{n'}$ (for $\eta=$argon 3p states)	$\mathfrak{L}^{3p}=1.50\times10^{-3}$ $n'=0.95$
Van der Waals parameter $-\lambda^{\eta}=(\lambda^{0\eta}+\lambda^{\eta 0})$ (negligible for $\eta=$argon 1s and 2s states)	$\lambda^{2p}=0.0769$ $\lambda^{3s}=0.0701$ $\lambda^{3p}=0.923$

The effect of neglecting interatomic exchange terms in calculating the spin-orbit parameter is negligible, since their only effect is to give S^4 corrections to the g shift.

The most pronounced exchange effects probably occur in the crystal-field parameter since the direct terms of this are of the same order of magnitude as the exchange terms. Phillips[28] has shown that for systems such as this the exchange terms may be comparable to the direct terms and considerable cancellation should occur. A large uncertainty, therefore, accompanies the calculation of the numerator of the expression for Λ^{ξ}, I_{ξ}, even if the exchange terms could be evaluated easily.

The Van der Waals parameters, $(\lambda^{0\eta}+\lambda^{\eta 0})$, are probably given reasonably well in this approximation for internuclear distances greater than six Bohr units. However, at smaller distances the overlap terms become increasingly important, but since the Van der Waals parameters have leading terms of order S^0, the overlap effects will not be as pronounced as for the crystal field parameter.

B. The g Shift

The g shift for a system of hydrogen in a rare gas is given by Eq. (6.3). The diagonal or isotropic elements are

$$\Delta g = -4\sum_\alpha \mathfrak{L}^\alpha S_{\alpha 0} \times[(0|w^\alpha L_z{}^2|\alpha)-\sum_\beta S_{\beta 0}(\beta|w^\alpha L_z{}^2|\alpha)]. \quad (7.1)$$

The corresponding result of Adrian's perturbation theory approach is

$$\Delta g = (4/3\bar{E}_H) S_{\alpha 0}{}^2 \lambda_{\alpha p\sigma} (\alpha|L_z{}^2|\alpha)\,, \quad (7.2)$$

where $\bar{E}_H$ is the average energy of the excited states of the hydrogen impurity, and $\lambda_{\alpha p\sigma}$ is the spin-orbit splitting constant for the rare gas p orbital.[5]

In both cases contributions to Δg come from rare-gas σ states since the overlap integrals are nonzero only for states with projected angular momentum, m_l, zero along the line joining the hydrogen and rare-gas nuclei. The result of a calculation of the projected components of the angular momentum for arbitrary magnetic field direction shows that for both the substitutional and the octahedral sites two thirds of the neighbors are effective in producing a g shift.

Figure 1 shows Δg for hydrogen in an octahedral site in argon as a function of internuclear distance. The agreement between the present result and Adrian's calculation is remarkable considering the vastly different theoretical techniques used. In addition to the theoretical curves, two "experimental" points are plotted using the assignments to undistorted lattice sites made by Foner *et al.*[2] One is for the octahedral site

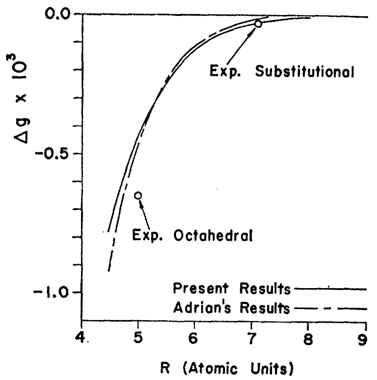

FIG. 1. The g-factor shift for a hydrogen atom trapped in an argon lattice at an octahedral site versus the nearest-neighbor distance, R. The circles represent experimental points according to the assignment of resonances made by Foner *et al.* (see Ref. 2).

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[27] The argon ground state wave functions of D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938), were used in these calculations.

[28] J. C. Phillips, J. Phys. Chem. Solids **11**, 226 (1959) and M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

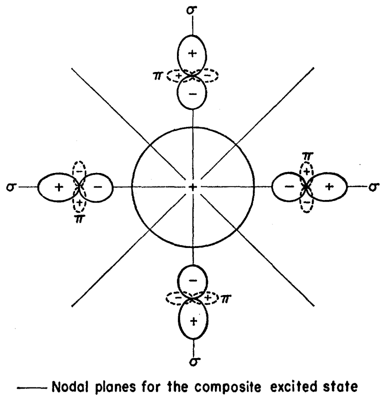

FIG. 2. A schematic plot of the charge density of the paramagnetic electron for a hydrogen impurity atom at an octahedral trapping site in a rare-gas solid. The solid curve shows the density of the "ground state" for which the spin-orbit interaction has been neglected. The dashed curve represents the excited state to which the "ground state" is coupled by the spin-orbit interaction. The solid curve has no azimuthal nodes, whereas the composite excited state has eight. The excited state of the crystal, therefore, corresponds to a diffuse g state centered about the impurity.

and the other is derived from the data for a substitutional site. The theory seems to agree reasonably with this assignment of trapping sites. Even better agreement would be expected if the effect of argon $2p$ states were included since the g shifts predicted by the present theory would be increased at smaller internuclear separations.

Both results are quadratic in wave function overlap, depend on the component of angular momentum parallel to the magnetic field, and are related to the spin-orbit effect in the rare-gas atoms by $\mathcal{L}^{\alpha}$ and $\lambda_{\alpha p\sigma}$, respectively. The essential difference between the two points of view is that here we consider the crystal as a whole, while previously just excited states for the isolated impurity were included in the perturbation treatment.

The result of making a perturbation-theory calculation for the crystal as a whole may be anticipated by considering the symmetry of the excited states admixed by the spin-orbit interaction to the electronic state having unpaired spin. The solid curve in Fig. 2 indicates schematically the charge distribution of the paramagnetic electron as determined by orthogonalized atomic functions for a hydrogen atom trapped in an octahedral site of a rare-gas solid. The figure is drawn for a plane passing through the impurity and four neighboring atoms. The outer shell electrons for the rare gas are assumed to be in $2p$ states, for simplicity, and the lobes of the distribution are labeled according to the sign of the wave function.

In the neighborhood of the impurity the distribution is spherically symmetric, but near the rare-gas atoms it has the character of a $p\sigma$ state centered on the individual rare-gas nuclei.[29] The strong electric field near the rare-gas nuclei cause a spin-orbit mixing with states having a π-like character centered on the same nuclei. These excited states are shown as dashed curves. The excited state of the crystal is the totality of these π-like states, and it has four aximuthal nodal planes intersecting at the impurity as indicated by the solid lines. This may be seen from a direct calculation or more simply from the symmetry of the site.[30] The excited state, therefore, corresponds, at the very least, to an $L=4$ or g state with the impurity nucleus as origin.

The results of a second-order perturbation-theory treatment considering the entire crystal would be the same as Eq. (7.2), but with an energy denominator given by a weighted average of the excitation energies of the system of impurity plus crystal. The lowest "impurity-like" state to contribute to this average would be the g state for principal quantum number five which, in the case of the free hydrogen atom, has an energy of 24/25 of the ionization energy.

The low-lying excited states of the impurity, therefore, cannot contribute to the perturbation theory sum over excited levels, and the energy denominator should be at least the ionization energy for the impurity in the crystal. Moreover, since the highly excited states of the impurity are spread out in the crystal they are probably more sensitive to the matrix material than to the details of the impurity, and a better choice for the average excitation energy denominator of Eq. (7.2) might be some energy characteristic of the rare-gas matrix. The latter conjecture is supported by the variational calculation since the "energy-denominator"-like term, $j_{\xi\xi}$, in the expression $\mathcal{L}^{\xi}\approx -i_{\xi}/j_{\xi\xi}$ for the spin-orbit variational parameter is associated with the host atom, rather than the impurity.[31]

A possible choice for the characteristic matrix energy would be the average excitation energy of the rare gas. For argon this is[32] 13.6 eV which is the same as the ionization energy of free hydrogen. Another choice is the energy of the first exciton peak of the rare-gas solid. Baldini finds this to be approximately 12.0 eV in argon.[33] All these energies are nearly the same as the average energy for hydrogen, viz., 11.9 eV, used in evaluating Eq. (7.2). Hence, for a hydrogen impurity no appreciable difference arises from the two points of view. However, the approximate equality between the excitation energies of the impurity and matrix atoms does not hold for the alkali metals, for which the average energies range from 3.62 to 2.64 eV.[32]

It might be argued that the present model would not apply to alkali impurities since the ground states of the alkali atoms would be greatly perturbed by the field of

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[29] $p\sigma$ is used to denote the p function directed along the line joining the nucleus of the rare-gas atom and that of the impurity atom. π states are directed along lines perpendicular to the axis of the σ states.

[30] For a pertinent discussion of the mixing of σ and π states and the selection rules involved in the v_k center see Ref. 13.

[31] A further discussion of the perturbation theory and variational results and speculations as to their relationship to an energy band picture of the solid will be included in a subsequent paper.

[32] In Ref. 5 the average excitation energy is taken as the average of the energy of the first excited state and the ionization energy.

[33] G. Baldini, Phys. Rev. **128**, 1562 (1962).

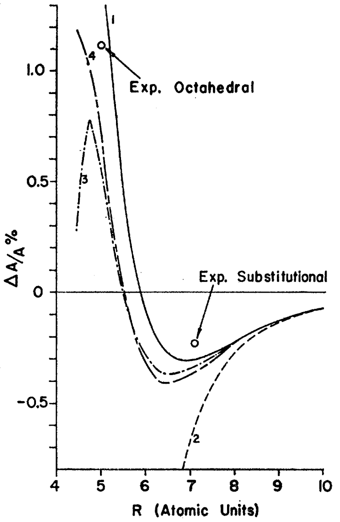

FIG. 3. The shift in hyperfine splitting for a hydrogen atom trapped in an argon lattice at an octahedral site versus the nearest neighbor distance, R. Curves 1, 2, and 3 summarize the present results. Curve 4 is Adrian's perturbation theory prediction. Curve 1 is based on a model of overlapping atoms interacting with a dipole-dipole Van der Waals force. Curve 2 includes, in addition, the effects of the non-exchange-corrected rare gas crystal field, and Curve 3 includes the effect of exchange corrections to the dipole-dipole approximation. The circles represent experimental points according to the assignment of resonances made by Foner *et al.* (see Ref. 2).

the rare-gas atoms and that, consequently, the unperturbed energy levels of the free impurity would have no significance in the solid. However, spectroscopic experiments indicate that there is little perturbation of the impurity atoms by the crystal environment. For example, electronic transitions of sodium in argon corresponding to the ${}^2S_{1/2}\rightarrow 3p$ and $4p\ {}^2P_{1/2\ 3/2}$ transitions in the free atom generally show shifts of only a few percent.[4] The largest fraction of these shifts doubtless arises from perturbations of the final p states, and it seems reasonable to assume that the ground state remains atomic in nature. Preliminary calculations on these systems indicate that the agreement of the present point of view with experiment[34] is better than the unmodified form of Eq. (7.2).

C. The Hyperfine Interaction

The shift in the hyperfine interaction arises from the orthogonalization of the wave functions in the solid, the effects of the crystal field, and the Van der Waals interaction.

The shift in hyperfine interaction due to orthogonalization (overlap) is given by Eq. (6.4); it may be compared with Adrian's result:

$$\frac{\Delta A_{\text{overlap}}}{A}=\sum_{\alpha} S_{0\alpha}^2. \tag{7.3}$$

The two equations differ by the addition term $-2\sum_\mu S_{\mu 0}\times(0|\delta(\mathbf{r}-R_0)|\mu)/(0|\delta(\mathbf{r}-\mathbf{R}_0|0)$ that occurs in the present result. The first part of Eq. (6.4) is just Adrian's result and arises from the increase in the hydrogen wave function at the nucleus, due to renormalization. The second part is the cross term between the hydrogen wave function, φ^0, and the argon functions, φ^μ, admixed by orthogonalization. Calculations indicate that at small internuclear distances this new term is important. For example, in the argon-hydrogen system at $R=5a_0$ (the octahedral site nearest-neighbor distance) it is 15% of the leading term, whereas at $R=10a_0$ it is only a 3% correction.

The shift in hyperfine interaction associated with the crystal field is a normalization correction to the electron density at the nucleus of the impurity. It is given by Eq. (6.5). This term has no counterpart in Adrian's study which is essentially a "point-ion" approximation. Numerical estimates of the crystal-field parameter, Λ^0, indicate that this effect is of order S^2, because the crystal field is localized within the atoms. However, it is difficult to estimate because of the cancellation occurring between direct and exchange terms in the expression for Λ^ξ and many-body screening effects.[28,35]

The Van der Waals, or correlation, effect produces two shifts. One is proportional to $(\lambda^{0\eta}+\lambda^{\eta 0})$ and is of order S^2. The other is a term of order S^0 in $(\lambda^{0\eta}+\lambda^{\eta 0})^2$. The first is given by Eq. (6.6). It does not arise in Adrian's study since it represents a cross term resulting from orthogonalization and the interaction between atoms. However, part of this term does appear in Jen's treatment of the hyperfine interaction.[34] This may be shown by a second-order perturbation theory treatment of the $1/r_{ij}$ interaction using antisymmetric wave functions. The result is a hyperfine-splitting shift proportional to the repulsive or Coulomb-exchange interaction similar to the second term of Eq. (6.6) in which $(\lambda^{0\eta}+\lambda^{\eta 0})$ plays the part of the reciprocal of the energy denominator. The first and third terms are exchange terms not having as simple an interpretation.

The $(\lambda^{0\eta}+\lambda^{\eta 0})^2$ term arises from the renormalization of the impurities wave function caused by the Van der Waals correction. It is given by Eq. (6.7) and should be compared with Adrian's result which is

$$\Delta A_{\text{vdW}}/A=-[1/(\bar{E}_H+\bar{E}_A)]E_{\text{vdW}}, \tag{7.4}$$

where $\bar{E}_A$ is the average excitation energy of argon and E_{vdW} is the Van der Waal energy for the interaction between a hydrogen atom and an argon atom.

In addition the difference in the Van der Waals interaction for the various higher s states mixed into the ground state by the hyperfine interaction leads to a shift in the hyperfine splitting. From the work of Adrian[5] and Herman and Margenau[16] this is

$$\Delta A_B/A=-(2/\bar{E}_H)E_{\text{vdW}}, \tag{7.5}$$

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[34] C. K. Jen, V. A. Bowers, E. L. Cochran, and S. N. Foner, Phys. Rev. 126, 1749 (1962).

[35] J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters 9, 215 (1962).

where $\bar{E}_H$ is the average excitation energy of hydrogen.

The numerical estimates for the shift in hyperfine splitting of a hydrogen atom in an argon lattice are given in Fig. 3 for both the present results and Adrian's treatment. Three curves are given for the present work. Each of these includes the shift due to orthogonalization, Eq. (6.4), the "quadratic" Van der Waals hyperfine shift, Eq. (6.7), and the Bender-Herman term as calculated by the perturbation theory treatment of Adrian, Eq. (7.5). The sum of these shifts is shown as curve 1. Curve 2 contains, in addition, the crystal-field correction, Eq. (6.5), and curve 3 contains the "linear" Van der Waals correction, Eq. (6.6), but no crystal-field correction. Curve 4 is Adrian's result.

Both curves 1 and 4 are in reasonable agreement with the experimental points and tend to substantiate the assignment of trapping sites. Curve 2 does not fit at all for interstitials and predicts too large a shift for substitutional impurities. Curve 3 fits reasonably for substitutional sites and possibly for interstitials, but its behavior for small internuclear distances seems unreasonable.

From the work of Phillips[28] it is reasonable to expect that the crystal-field parameter is much smaller than the single direct term calculated here. In fact, the cancellation of direct and exchange terms probably reduces it by at least an order of magnitude if not more. This would explain the disagreement of curve 2 with experiment even at relatively large internuclear distances. If we assume complete cancellation, i.e., set $\Lambda^0=0$ and include the linear Van der Waals term, there is reasonable agreement with experiment at the substitutional site (curve 3). However, the linear Van der Waals term, which is negative, increases rapidly below 6 Bohr units as the exchange dipole matrix elements become large and causes curve 3 to reverse in direction.

Thus, we find that both the relatively simple pictures of the hyperfine shift that neglect crystal field and linear Van der Waals terms give good agreement with experiment. Attempts to refine this simple picture only worsen the agreement, particularly at small internuclear distances. This indicates that at the substitutional-site-distances corrections to an overlap-plus-Van der Waals force calculation are small, but that at smaller distances the corrections become the dominant terms, and the model is no longer applicable.

At these smaller separations the solution to the problem of calculating the wave functions must be reexamined. As previously pointed out by Adrian, the multipole expansion for the Van der Waals energy no longer holds. Furthermore, the simple idea of a crystal field is considerably modified by exchange and many-body screening effects.[28,35] The tight-binding model of atomic one-electron functions with small corrections for crystal field and electron correlation probably can be pushed further using more flexible variational functions in the general framework given here, but the $1/r_{ij}$ interaction must be treated in a better approximation and the exchange effects included at all steps.

VII. CONCLUSION

In this study a calculation correct to second order in wave-function overlap has been made for the ground-state wave function and electron-spin-resonance parameters of a paramagnetic impurity in a rare gas. Starting from a one-electron, tight-binding, static-lattice picture of the impurity-doped crystal, the Pauli principle is satisfied by using an antisymmetric crystal wave function. This wave function is then modified by the addition of variational terms of the correct symmetry to account for the perturbations on the tight-binding approximation due to the crystal field, spin-orbit, and Van der Waals interactions.

The results show that, if there is no overlap, the effects of the individual perturbations due to the crystal environment are independent. If there is appreciable overlap, the individual effects are coupled and must be calculated simultaneously. In this case, the intra-atomic potentials of the atoms neighboring the impurity must be taken into account as a crystal field, and the Van der Waals effect must be calculated for overlapping charge distributions.

For a paramagnetic center in a relatively weak crystal field, the g shift arises because the electronic wave functions, centered on the impurity, overlap neighboring atoms in which there is appreciable spin-orbit interaction. The g shift is independent of crystal field and correlation effects, and appears to be the most reliably calculated parameter for a tight-binding center of known geometry in a molecular crystal.

The shift in the hyperfine interaction arises from (1) the orthogonalization of the wave functions for the electrons in the solid, (2) the crystal field, and (3) the Van der Waals interaction. Since this shift is the sum of three quantities, it is less reliably calculated than the g shift because cancellation occurs. Indeed, at small separations, the predicted shifts are the difference of two very large numbers which are, at best, known only approximately.

It is found that the relatively simple picture of slightly overlapping atoms undergoing a multipole Van der Waals interaction gives good results for substitutional sites in rare-gas crystals, but that at interstitial sites it breaks down; and the shifts in the hyperfine interaction cannot be accurately estimated without including crystal field and all exchange effects correctly.

It should be noted that the difficulties encountered in making the crystal field and Van der Waals calculations for interstitial impurities have negligible effect on the g-shift calculations. In the case of the crystal field, the primary effect is a change in the impurity's s-state radial distribution which, of course, doesn't affect the magnetic properties directly. Likewise, the electron correlation correction to the wave function leads to a

g shift only in the equivalent of fourth-order perturbation theory and is negligible. Hence, although it is difficult to calculate the hyperfine interaction accurately for interstitial sites, the g shift should be given to a good approximation by Eq. (7.1) or Eq. (7.2) if $\bar{E}_H$ is replaced by the appropriate average excitation energy for the system of rare-gas crystal plus impurity.

At the present time the methods outlined here are being applied to the calculation of the g shift for the alkali metals trapped in rare gas solids. The results will be published as soon as the numerical work is completed.

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APPENDIX

As an example of the calculation of the energy equation coefficients, an outline of the derivation of the quantities determining Λ^ξ will be given. The general method is to start with the Hamiltonian and replace the Löwdin functions by their series representations in atomic functions.

To simplify the derivation, the Hamiltonian is written symbolically as

$$\mathcal{H}'=W+\textstyle\sum_i H_i+\sum'_{i<j} G_{ij}\,, \qquad \text{(A1)}$$

where W, H_i, and G_{ij} are, respectively, those portions of the Hamiltonian depending on no electron coordinates, on one coordinate $\mathbf{r}_i$, and on two coordinates $\mathbf{r}_i$, and $\mathbf{r}_j$. The prime on the double summation indicates that all terms having the indices i and j equal are omitted.

A. The I_ξ Term

Using the expansion of Eq. (A1) and substituting in Eq. (5.3), we have

$$\begin{aligned} I_\xi=&\langle\xi_i|v_i{}^\xi H_i|\xi_i\rangle \\ &+\sum_{\eta\neq\xi}\langle\xi_i\eta_j|v_i{}^\xi G_{ij}|\xi_i\eta_j\rangle-\langle\xi_i\eta_j|v_i{}^\xi G_{ij}|\eta_i\xi_j\rangle \\ &-\sum_\eta\langle\xi|v^\xi|\eta\rangle[\langle\eta|H|\xi\rangle+\sum_{\rho\neq\eta}\langle\eta_i\rho_j|G_{ij}|\xi_i\rho_j\rangle \\ &\qquad -\langle\eta_i\rho_j|G_{ij}|\rho_i\xi_j\rangle]. \qquad \text{(A2)}\end{aligned}$$

Since we are mainly concerned with the impurity atom, we need only consider the case for ξ the $1s$ hydrogen state. Then we profit from the fact that since the hydrogen atom has only one electron, all exchange terms involving φ^ξ are between electrons on different atoms and so are of order S^2.

Using these facts we find on substitution of the explicit forms for H_i and G_{ij} and identification of atomic and crystal potentials the result

$$\begin{aligned} I_0=&(0|v^0\bar{\Sigma}V_0|0)-\sum_\eta(0|v^0|\eta)(\eta|\bar{\Sigma}V_0|0) \\ &-\tfrac{1}{2}\sum_\alpha S_{0\alpha}\{(0|v^0\bar{\Sigma}V_\alpha|\alpha)+(\alpha|v^0\bar{\Sigma}V_0|0) \qquad \text{(A3)} \\ &-(0|v^0|0)[(0|\bar{\Sigma}V_\alpha|\alpha)+2(\alpha|\bar{\Sigma}V_0|0)] \\ &+[(0_i0_j|v_i{}^0r_{ij}{}^{-1}|0_i\alpha_j)-(0_i0_j|v_i{}^0r_{ij}{}^{-1}|\alpha_i0_j)]\}.\end{aligned}$$

Here the atomic eigenvalues have canceled, leaving only matrix elements of the crystal field potential.

The first two terms of Eq. (A3) are just the "zero-order" term in the Löwdin expansion. The next three terms and half of the sixth result from replacing ϕ^0 in the bra or ket of the term $\langle 0|v^0\mathcal{H}'|0\rangle$ and $\langle 0|\mathcal{H}'|0\rangle$ with $\phi^0=\varphi^0-\frac{1}{2}\sum\alpha S_{0\alpha}\varphi^\alpha+\cdots$. The other half of the sixth term, $(\alpha|\bar{\Sigma}V_0|0)$, comes from replacing ϕ^η with $\phi^\eta=\varphi^\eta-\frac{1}{2}S_{\eta 0}\varphi^0$ in the first matrix element of $\Sigma_\eta\langle 0|v^0|\eta\rangle\times\langle\eta|\bar{\Sigma}V_0|0\rangle$. The remainder of the equation results from expanding the bra of the second and third terms of Eq. (A2). Expansion of ϕ^η in the ket gives nothing since the resulting terms cancel identically.

B. The $J_{\xi\eta}$ Terms

The leading term in I_ξ is itself proportional to S^2, so we need to find $J_{\xi\xi}$ to order S^0. During its evaluation, one term that arises is of the form

$$\begin{aligned} T=&(\xi_i|v_i{}^\xi[-\tfrac{1}{2}\nabla_i{}^2-Z_Ir_{iI}{}^{-1} \\ &+\sum_{\eta\neq\xi}{}^\xi(\xi_j|r_{ij}{}^{-1}|\xi_j)+\bar{\Sigma}V_\xi]v_i{}^\xi|\xi_i). \qquad \text{(A4)}\end{aligned}$$

Expansion of the ∇^2 term, integration by parts, and identification of the crystal field and atomic potentials gives

$$\begin{aligned} T=&\epsilon_\xi(\xi|(v^\xi)^2|\xi)+\tfrac{1}{2}(\xi|\boldsymbol{\nabla}v^\xi\cdot\boldsymbol{\nabla}v^\xi|\xi) \\ &+(\xi|v^\xi\bar{\Sigma}V_\xi v^\xi|\xi), \qquad \text{(A5)}\end{aligned}$$

where ϵ_ξ is the energy eigenvalue for the atomic state φ^ξ. The terms involving the atomic eigenvalues cancel against similar terms in the complete expression, and the terms in the crystalline potential are dropped since they are of order S^2.

The final expressions are

$$J_{\xi\xi}=\tfrac{1}{2}(\xi|\nabla v^{\xi}\cdot\nabla v^{\xi}|\xi), \tag{A6}$$

and

$$\begin{aligned}J_{\xi\eta}&=0 \text{ if } \xi \text{ and } \eta \text{ are on different atoms,}\\ &=(\xi_i\eta_j|v_i^{\xi}[r_{ij}^{-1}-(\eta_k|r_{ik}^{-1}|\eta_k)\\ &\quad-(\xi_k|r_{jk}^{-1}|\xi_k)]v_j^{\eta}|\xi_i\eta_j)+(\xi_i\eta_j|v_i^{\xi}v_j^{\eta}|\xi_i\eta_j)\\ &\qquad\times(\xi_i\eta_j|r_{ij}^{-1}|\xi_i\eta_j),\end{aligned}$$

if ξ and η are on the same atom.

C. The $K_{\xi\eta}$ Term

To evaluate this term to order S^0, the Hamiltonian may be approximated by the one-electron operator made up of approximate one-electron atomic Hamiltonians, $\mathcal{H}_0$, plus the crystal-field interaction without exchange, $\sum' V$. Writing the spin-orbit term, h_{so}, separately from the atomic terms, we have,

$$\mathcal{H}'\approx\sum_i\mathcal{H}_0(\mathbf{r}_i)+h_{\text{so}}(\mathbf{r}_i)+\sum' V(\mathbf{r}_i). \tag{A7}$$

From Eq. (5.3) we have for this Hamiltonian

$$\begin{aligned}\sum_\eta K_{\xi\eta}\mathcal{L}^{\eta}=&\mathcal{L}^{\xi}\tfrac{1}{2}(\xi|\nabla v^{\xi}\cdot\nabla w^{\xi}(\mathbf{L}\cdot\boldsymbol{\sigma})|\xi)+\mathcal{L}^{\xi}(\xi|v^{\xi}w^{\xi}(\mathbf{L}\cdot\boldsymbol{\sigma})\mathcal{H}'|\xi)-\sum_\eta\mathcal{L}^{\eta}(\xi|v^{\xi}w^{\eta}\mathbf{L}\cdot\boldsymbol{\sigma}|\eta)(\eta|\mathcal{H}'|\xi)\\ &-\sum_\eta\{\mathcal{L}^{\xi}(\xi|v^{\xi}\mathcal{H}'|\eta)(\eta|w^{\xi}\mathbf{L}\cdot\boldsymbol{\sigma}|\xi)-\sum_\rho\mathcal{L}^{\xi}(\xi|v^{\xi}|\rho)(\rho|\mathcal{H}'|\eta)(\eta|w^{\xi}\mathbf{L}\cdot\boldsymbol{\sigma}|\xi)+\mathcal{L}^{\xi}(\xi|v^{\xi}|\eta)(\eta|\mathcal{H}'w^{\xi}\mathbf{L}\cdot\boldsymbol{\sigma}|\xi)\\ &-\sum_\rho\mathcal{L}^{\rho}(\xi|v^{\xi}|\eta)(\eta|w^{\rho}L\cdot\sigma|\rho)(\rho|\mathcal{H}'|\xi)+\mathcal{L}^{\eta}(\xi|v^{\xi}|\xi)[(\eta|w^{\eta}\mathbf{L}\cdot\boldsymbol{\sigma}\mathcal{H}'|\eta)-\sum_\rho(\eta|\mathcal{H}'|\rho)(\rho|w^{\eta}\mathbf{L}\cdot\boldsymbol{\sigma}|\eta)]\\ &+\mathcal{L}^{\eta}(\eta|w^{\eta}\mathbf{L}\cdot\boldsymbol{\sigma}|\eta)[(\xi|v^{\xi}\mathcal{H}'|\xi)-\sum_\rho(\xi|v^{\xi}|\rho)(\rho|\mathcal{H}'|\xi)]\}.\end{aligned} \tag{A8}$$

Since we are interested in the case for φ^{ξ} an impurity function, the matrix elements on the right-hand side are either of order S^2 because they represent exchange terms, or because w^{ξ} for hydrogen is zero to order S^2. An even more general argument holds for many of the terms which must vanish because of the sum over closed shells. The cross terms with $\mathcal{L}^{\eta}$, therefore, make no contribution to Λ^{ξ}.

D. The $L_{\xi,\eta\rho}$ Terms

Since this term involves the function $u_{ij}^{\xi\eta}$ approximating the Hamiltonian by (A7) would suppress terms involving the Van der Waals interaction. However, since we seek only a small correction to I_{ξ} we can approximate the Hamiltonian as the sum of the atomic Hamiltonians and the interactions between electrons expanded as a multipole series. From the work of Brooks[36] one would presume that the dipole-dipole term would be sufficient to estimate the correction. Thus, we shall use

$$\mathcal{H}'\approx\sum_i\mathcal{H}_0(\mathbf{r}_i)+\tfrac{1}{2}\sum'_{i,j}v_{ij}, \tag{A9}$$

where the interaction v_{ij} is the dipole-dipole interaction between different atoms. It has the same form as that chosen for $u_{ij}^{\xi\eta}$. Notice that we exclude intra-atomic terms by requiring that $\mathbf{r}_i$ and $\mathbf{r}_j$ be coordinates of functions centered on different atoms.

In the "u" notation the cross term in the energy is

$$\begin{aligned}\sum_\xi\sum_\eta\sum_{\rho>\eta}&2L_{\xi,\eta\rho}\Lambda^{\xi}(\lambda^{\eta\rho}+\lambda^{\rho\eta})\\ &=2\langle u_1|\mathcal{H}'|u_3\rangle-2\langle u_0|\mathcal{H}'|u_0\rangle\langle u_1|u_3\rangle\\ &\quad-4\langle u_1|u_0\rangle\langle u_0|\mathcal{H}'|u_3\rangle-4\langle u_3|u_0\rangle\langle u_0|\mathcal{H}'|u_1\rangle\\ &\qquad+8\langle u_1|u_0\rangle\langle u_0|u_3\rangle\langle u_0|\mathcal{H}'|u_0\rangle.\end{aligned} \tag{A10}$$

The free atomic energy eigenvalues, ϵ_ν, will cancel in the first two terms except for the gradient term in the matrix element $\langle u_1|\mathcal{H}'|u_3\rangle$. However, these are zero because of the oddness of the undifferentiated part of $u_{ij}^{\xi\eta}$. The ϵ_ν's don't enter into the second set of terms because of the oddness of $u_{ij}^{\xi\eta}$. Furthermore, the second, fourth, and fifth terms are zero for the same reason. The only terms that remain are in v_{ij} and, after simplification, the final result for the Van der Waals correction to the crystal-field parameter is

$$\begin{aligned}\sum_\eta\sum_{\rho>\eta}&L_{\xi,\eta\rho}(\lambda^{\eta\rho}+\lambda^{\rho\eta})\\ &=\sum_{\rho\neq\xi}(\lambda^{\xi\rho}+\lambda^{\rho\xi})\{(\xi_i\rho_j|u_{ij}^{\xi\rho}v_{ij}v_i^{\xi}|\xi_i\rho_j)\\ &\quad-(\xi_i\rho_j|u_{ij}^{\xi\rho}v_{ij}|\xi_i\rho_j)(\xi|v^{\xi}|\xi)\}\\ &\quad-\sum_\eta\sum_{\rho>\eta}(\lambda^{\eta\rho}+\lambda^{\rho\eta})(\eta_i\rho_j|u_{ij}^{\eta\rho}v_{ij}|\eta_i\rho_j)(\xi|v^{\xi}|\xi).\end{aligned} \tag{A11}$$

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[36] F. C. Brooks, Phys. Rev. 86, 92 (1952).