A VARIATIONAL THEORY OF PARAMAGNETIC IMPURITIES
IN VAN DER WAALS CRYSTALS

by

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PRÉCIS

In this investigation an attempt has been made to develop a consistent method of calculating the wave function of an impurity center in a molecular crystal and from this to predict its observable electron spin resonance properties. Specifically the theory has been applied to the system of atomic hydrogen in solid argon.

Starting from the one-electron, tight-binding, static-lattice picture of the impurity-doped crystal, an orthonormal set of one-electron functions for the crystal is formed by making a unitary transformation on the Hartree-Fock free atomic wave functions. The wave function for the crystal is then formed as the antisymmetrized product of these starting 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 or electron correlation effect.

The variational parameters necessary for the specification of the impurity's properties are determined by minimization of the crystal energy. The spin resonance parameters may then be calculated in terms of the free atomic wave functions and the variational functions.

The results show that the g-shift is the most easily calculated quantity for a paramagnetic center in a molecular crystal. It arises from the overlap of an electron centered on the impurity with atoms of the host crystal in which there is a spin-orbit interaction. The shift in the g factor is always negative.

The hyperfine splitting is altered by three things: the overlap, the crystal field and the Van der Waals interaction. Generally, the overlap leads to an increase in the hyperfine splitting while the crystal field and the Van der Waals interaction tend to reduce it. At large internuclear separations the latter effects dominate giving negative shifts while at small internuclear separations the former effect dominates and leads to positive shifts.

It is found that provided there is no overlap, it is a good approximation to calculate the various effects of the crystal environment on the impurity center and then add to find the net effect. However, this procedure is not justified if there is appreciable overlap. In this case, the effect of intra-atomic potentials and interatomic exchange matrix elements must be taken into account.

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CHAPTER I

INTRODUCTION

Recent developments in solid state experiments, including electron and nuclear spin resonance work¹, luminescence studies², and other precise optical measurements on solids³, have spurred theoretical study of the electronic structure of isolated impurity atoms in crystals.

In the theoretical treatment of the electronic structure of solids there are two well-defined starting places for calculation: the Bloch (free electron) model^{4,5} and the Heitler-London (tight binding) model^{4,6}. In the first the electrons are assumed to be moving like almost free particles in the potential well of the solid; in the second they are pictured as being tightly bound to almost isolated atoms.

The solution to the electronic structure of a real solid lies between these extremes, and, in some cases, may be treated as a small perturbation on one or the other. For example, the structure of shallow electron traps in semi-conductors has been shown to be given very well by a perturbation on the Bloch scheme in which the donor impurity is considered to be a positive point charge in a polarizable medium of high dielectric con-

stant.⁷ At the other extreme, there are cases in which the impurity centers are essentially atomic in character; examples are luminescence of centers in which transitions occur in inner shells⁸, electron spin resonance of certain impurities in both ionic and molecular crystals^{9,10,11,12,13}, and optical transitions of impurities in rare gas crystals.^{3,14}

The present work outlines an attempt to make a "first principles" calculation of the ground state wave function of one of these tight binding impurity centers. Specifically, the case of atomic hydrogen in solid argon is treated, with emphasis on its electron spin resonance properties. The calculation is "first principles" in the sense that recourse is not made to experimentally determined quantities such as polarizabilities or oscillator strengths and that the major effects of the crystal environment are calculated simultaneously so that cross terms involving different crystal effects are retained. In previous work, the additivity of the various crystal perturbations has been assumed^{14,15} and experimental data have been used to evaluate parameters in the models.^{16,17}

In general it is to be expected that the electron spin resonance properties of tight binding centers will

be closer to free atomic values than the optical properties will be. This follows because the usual resonance experiments depend on the ground state alone, whereas optical transitions involve, in addition, the more weakly bound and hence more perturbed excited states.

Accordingly the calculation of the electron spin resonance properties was undertaken as a starting place for the investigation of the argon-hydrogen system. With minor revisions, the theory should be generally applicable to impurities with one electron outside a closed shell and to other matrix materials. Furthermore, from the theory developed, calculations for excited states could be made, but with greater difficulty in calculating overlap effects.¹⁸

In systems of this sort, a study of the Hamiltonian shows that the most important contributions to the interaction of the impurity with the host crystal come from the Van der Waals or electron correlation effect, the coulomb interaction of electrons with the shielded nuclear charge of neighboring atoms, and the spin-orbit interaction, all of which are small compared with the separation between the ground state energy and excited atomic states.

Since the electronic states are essentially

atomic, we shall use a one-electron, tight binding approximation. Also, because the rare gases solidify at very low temperatures, the neglect of lattice vibrations would seem valid in calculating electron distributions. Thermal oscillation would, of course, have to be considered in a spin relaxation study.

Starting from this one-electron, tight binding, static lattice picture, we include the interactions among atoms as perturbations, allowing them to modify the atomic wave functions of both the impurity and the host lattice to form the crystalline one-electron functions. Then the total crystal wave function is formed as the antisymmetrized product of these modified functions. From this, the shift in ground state energy and the spin resonance properties may be calculated.

To carry out this program, each of the interactions between atoms is taken into account by adding an appropriate variational function to the individual wave functions. The total energy of the crystal is then calculated and minimized to give the best variational wave functions. Using these "crystal" wave functions the expectation value of the interactions with a magnetic field is calculated to give experimentally observable resonance properties.

In this study the three major interactions are taken into account simultaneously, and from the formalism it is clear how exchange and the cross terms arising from the various quantities in the Hamiltonian appear in the final energy. This allows the determination of the several variational functions so that they are consistent with each other and the Pauli principle to second order in the overlap integrals.

Here we have used the overlap, that is the integral of the electronic wave function of the impurity times that of an electron centered on a neighboring atom, as a measure of the degree of approximation. These overlap integrals are related to the repulsive exchange interaction in the solid and are generally small compared to unity. Representative values for the case of hydrogen in argon are of 0.1 or less. Overlap integrals are a good measure of the degree of approximation since their magnitude depends on the amount of interatomic exchange present in the solid. By "keeping terms to second order in overlap", we mean that we include in the calculation matrix elements involving permutations with one interchange of electronic coordinates from a function centered on one atom to one centered on a neighboring atom. If the overlap is very large, for example, as in some molecules, interatomic

exchange becomes more important and matrix elements involving additional interchanges must be kept. This second-order approximation is discussed further in Appendix B.

CHAPTER II

A QUALITATIVE PICTURE OF TIGHT BINDING PARAMAGNETIC CENTERS

1. Crystalline Perturbations

A physical idea of how the interactions within a rare gas crystal operate can be obtained by considering the changes in the wave function of a single impurity atom placed in a matrix of electrically neutral atoms. Here four things are important: a) the Pauli principle and the three major perturbations on the atomic Hamiltonian, b) the Van der Waals interaction, c) the crystal field, and d) the spin-orbit force.¹⁹

a. The effect of the Pauli principle can be seen by orthogonalizing the impurity atom's wave function to those of the neighbors. This leads to a decrease in the impurity's wave function within the neighboring atoms and a consequent compression of the wave function inward towards the impurity center.

b. The Van der Waals force, on the other hand, leads to an outward extension of the impurity atom's wave function. In perturbation theory this can be seen roughly from the fact that more diffuse excited states are added to the ground state by this additional term in

the Hamiltonian.

c. Similarly, the electrostatic attraction of the only partially shielded nuclear charge of the neighboring atoms spreads out the electronic wave function of the impurity.

d. The motion of electrons relative to the atomic electric fields within the crystal leads to an effective magnetic field as seen by the electrons. The electronic moments interact with this field yielding the spin-orbit interaction. Rigorously this arises in Dirac's relativistic treatment of electrons and for spherically symmetric potentials has the familiar form of a function of position times $\underline{L} \cdot \underline{\sigma}$ where $\underline{L}$ is the orbital angular momentum operator and $\underline{\sigma}$ is the Pauli spin operator. Since $\underline{L} \cdot \underline{\sigma}$ is not diagonal in the L, S, m_L, m_S scheme, this perturbation mixes angular momentum and spin states.

In free atomic hydrogen, there is no spin-orbit effect in the ground state since it is an s function. However, when included as an impurity in an argon crystal, overlap of the electronic wave functions leads to the admixture of argon p states to the hydrogen 1s state. When the impurity's electron is "in" one of the admixed argon p states it experiences a spin-orbit effect with the consequent admixture of other spin and angular

momentum states.

2. The Spin Resonance Parameters

The results of electron spin resonance experiments may be described in terms of an effective Hamiltonian. This "spin Hamiltonian" gives the interaction of the spin as if it were a free spin, but with "effective" coefficients for the interactions of the electronic spin with the magnetic field and the other spins, both electronic and nuclear, in the crystal.^{20,21}

For example, for a singlet state the spin Hamiltonian is²⁰

$$\mathcal{H}_s = \frac{\beta}{2} \underline{H} \cdot \underline{\vec{g}} \cdot \underline{\sigma} + \frac{A}{2} \underline{I} \cdot \underline{\sigma} - \beta^2 \underline{H} \cdot \underline{\vec{\lambda}} \cdot \underline{H} + \underline{\sigma} \cdot \underline{\vec{D}} \cdot \underline{\sigma} \quad (2-1)$$

where $\underline{\vec{g}}$, $\underline{\vec{\lambda}}$ and $\underline{\vec{D}}$ are tensors. The first term represents the interaction of the spin and the magnetic field and the second is the hyperfine or nuclear spin-electron spin interactions. The third term is a quadratic field term and the fourth is the spin-spin interaction.

We shall be concerned only with the gyromagnetic ratio or g-factor, $\underline{\vec{g}}$, and the hyperfine splitting factor, A. The values of $\underline{\vec{g}}$ and A in the spin Hamiltonian are effective ones for the crystal and are the sum of the free atomic values of $\underline{\vec{g}}$ and A plus shifts introduced

by the crystal environment.

Roughly the effect of the crystal on the impurity atom's electron spin resonance properties may be seen as follows. The first three "perturbations" combine to produce a shift in the hyperfine interaction of the impurity. Orthogonalization tends to compress the impurity wave function while the Van der Waals interaction and the crystal field effects tend to extend it. Since the hyperfine splitting for s states is directly proportional to the unpaired spin density at the nucleus of the atom in question, the net result of this compression and extension is to produce a shift in hyperfine splitting, A . This shift may be either positive or negative, depending on what terms are dominant.

In the case of hydrogen in argon, no important hyperfine shift arises from spin-orbit effects, since the spin-orbit effects are appreciable only near the argon nuclei, whereas the hyperfine splitting arises from interactions with the hydrogen's nucleus.

The spin-orbit effect on the other hand, gives rise to a shift in the g-factor. In the solid overlap admixes argon p functions to the hydrogen atom's s function. When the impurity's electron is in one of these admixed states, it must be described not by a

projected spin quantum number $\sigma_M = \pm 1$, but with the quantum number J since $\underline{L}$ and $\underline{S}$ are coupled by the $\underline{L} \cdot \underline{S}$ interaction. As a consequence, the g-factor is decreased from the free electron value.

The Van der Waals and crystal field interactions do not produce any g shift except inasmuch as they introduce higher angular momentum states into the impurity's wave function. For example, in a cubic site we might expect $L = 4$, i.e., g states admixed. However, in molecular crystals the crystal field is localized within the atoms and its effects are shown to be negligible in the approximation used in this study (see Appendix D, section 3b).

CHAPTER III

HISTORICAL SURVEY

A considerable body of experimental data on the electron spin resonance properties of atomic hydrogen trapped in rare gases has become available largely through the efforts of Foner, Cochran, Bowers and Jen.^{10,11} Further study of these paramagnetic centers is presently underway by Wyman.²²

In the work of Foner et al.¹¹, samples were prepared by two methods. In the first, hydrogen atoms from an electrical discharge in H_2 and the rare gas atoms were simultaneously deposited on a sapphire rod cooled by liquid helium. In the second, an easily dissociated hydrogen compound such as HI, H_2O or NH_3 and the rare gas were deposited. Subsequently, this frozen mixture was exposed to ultraviolet light and the hydrogen compound decomposed to yield atomic hydrogen. The ratio of rare gas to photosensitive compound was reported to be typically 100:1. The samples were some 0.5 mm thick and, after preparation, the sapphire rod with the sample was placed in a microwave cavity for the resonance observations.

A summary of the data of Foner et al.¹¹ is given in Table I. There are two main features of these results.

TABLE I. Observed Paramagnetic Resonance Constants for Hydrogen Atoms in Argon*

Matrix	Experiment	A(Mc/sec)	$\frac{\Delta A}{A}$ (%)	g_J	$-\Delta g_J$
Free State ^{23,24}		1420.40573(5)		2.002256(24)	
Argon	Deposition	1413.82(40)	-0.46	2.00220(8)	0.00006
	Photolysis A	1413.82(40)	-0.46	2.00220(8)	0.00006
	" B	1416.31(80)	-0.29	2.00224(12)	0.00002
	" C	1436.24(40)	+1.15	2.00161(8)	0.00065

* The numbers in parentheses indicate experimental and/or conversion errors in the last figures of the associated values.

The first is that the shifts in the g factor and the hyperfine interaction from the free atomic values is extremely small. The second is that there are up to three sharply defined resonances for a single system. The resonances labeled A and C were consistently observed in photolysis experiments while resonance B was observed only occasionally in photolysis of HI in argon.

The first of these indicates that there is little interaction between the hydrogen and the rare gas in which it is trapped. The second suggests that there are certainly two and perhaps three nonequivalent trapping sites. This last conclusion is supported by the observation that as the samples were warmed up, first one and then another line disappeared, indicating that the centers responsible for the resonances are stable in different temperature ranges and are intrinsically different. The possibility that the dissociation product of the hydrogen compound in the photolysis experiments could be responsible for some additional lines has been ruled out by the experimenters. They argue that neither the g shift nor the hyperfine splitting values correspond to the observed properties of possible unwanted dissociation products.

F. J. Adrian¹⁵ has undertaken a semiquantitative

theoretical study of the results of Foner et al. In this work Adrian took into account the effects of Van der Waals interactions, spin-orbit effect and overlap of the wave functions. He treated the effects separately and added the shifts produced by each to get the net shifts. To estimate the Van der Waals interaction and spin-orbit effects, perturbation theory was used. The shifts produced were related to the polarizabilities of the interacting atoms and the free atom spin-orbit splitting respectively. Overlap effects were taken into account by using Schmidt orthogonalization.

It was found that the g shift was given entirely by the spin-orbit effect. The hyperfine interaction was changed by both the Van der Waals interaction and the overlap correction. A summary of this work is given in Appendix E.

In general the results of Adrian's calculations agree rather well with experiment and enable one to make an assignment of the various resonances to possible trapping sites in the rare gas lattice.

On the other hand, the wave function used in his calculation is not antisymmetric and the effects of crystal fields are not included. Furthermore, the calculation is not shown to be consistent to a given order

in the overlap between charge clouds. It is to include these refinements and to place the calculation on a consistent basis that the present work was undertaken.

CHAPTER IV

NATURE OF TRAPPING SITES IN RARE GAS CRYSTALS

The rare gases crystallize as face-centered cubic lattices. Foner et al.¹¹ have pointed out that for this structure an impurity atom can be in only three stable positions. These are the substitutional site and two interstitial positions--an octahedral site at the center of the face-centered cube or a tetrahedral one near any corner of the face-centered cubic structure. These are shown in Figure 1.

Table II gives the number on nearest, N_{nn} , and next nearest neighbors, N_{nnn} , as well as their distances from the impurity, d_{nn} and d_{nnn} respectively, for these sites in the undistorted lattice. In addition the table also gives the argon 3p - hydrogen 1s overlap integral

$$\int \varphi_{\text{Argon } 3p\sigma}^* \varphi_{\text{Hydrogen } 1s} d\tau = S_{A3p\sigma, H1s} \quad (4-1)$$

and two parameters measuring the importance of the next nearest neighbor interactions to those of the nearest neighbors. The unit of length is $a_0 = \hbar^2/me^2$.

In the case of the Van der Waals interaction the ratio of the energy contribution by the two sets of neighbors is approximately $\frac{N_{nnn}}{N_{nn}} \left(\frac{d_{nn}}{d_{nnn}} \right)^6$. Both the

- Lattice atoms and substitutional sites
- Octahedral sites
- ⊗ Tetrahedral sites

Figure 1.

Trapping sites in a face-centered cubic lattice. All the substitutional and octahedral sites are shown, but only two tetrahedral sites are indicated.

TABLE II. Properties of Trapping Sites in an Undistorted Argon Lattice

Site	Neighbor	Number	Distance	$s_{3p\sigma, 1s}$ Overlap	$\frac{N_{nnn}}{N_{nn}} \left(\frac{d_{nn}}{d_{nnn}} \right)^2$	$\frac{N_{nnn}}{N_{nn}} \left(\frac{s_{nnn}}{s_{nn}} \right)^2$
Substitutional	nearest	12	$\frac{a}{\sqrt{2}} = 7.09a_0$	0.0226	0.031	0.004
	next nearest	6	$a = 10.03a_0$	0.002		
Octahedral (Interstitial)	nearest	6	$\frac{a}{2} = 5.01a_0$	0.108	0.049	0.004
	next nearest	8	$\frac{\sqrt{3}}{2}a = 8.68a_0$	0.006		
Tetrahedral (Interstitial)	nearest	4	$\frac{\sqrt{3}}{4}a = 4.34a_0$	0.170	0.061	0.0066
	next nearest	12	$\frac{\sqrt{11}}{4}a = 8.34a_0$	0.008		

crystal field or coulomb and spin-orbit interactions are proportional to the square of the overlap integral. So for these interactions the ratio is $\frac{N_{nnn}}{N_{nn}} \left(\frac{S_{nnn}}{S_{nn}} \right)^2$. In all cases these ratios are less than a few percent and we shall consequently neglect all but the nearest neighbors in calculating the effect of the crystal on an impurity.

CHAPTER V

THE HAMILTONIAN

To determine the spin resonance parameters, we must find the ground state wave function of the impurity-doped crystal. We shall do this in the adiabatic approximation due to Born and Oppenheimer.⁴ In this scheme, we treat the nuclear coordinates as parameters in the electronic wave function realizing that the nuclei act almost like bodies at rest relative to the fast-moving electrons.

In the adiabatic approximation, the Hamiltonian for the electronic motion is given by the complete Hamiltonian operator for the crystal less the kinetic energy of the nuclei. For a system of N nuclei with charge $Z_J e$, $J = 1 \dots N$ and $\sum_J Z_J$ electrons, we shall consider the Hamiltonian

$$\begin{aligned}
 \mathcal{H} = & \frac{-\hbar^2}{2m} \sum_i \nabla_i^2 + \\
 & + e^2 \sum_I \sum_J \frac{Z_I Z_J}{|\underline{R}_I - \underline{R}_J|} + e^2 \sum_{i < j} \frac{1}{|\underline{r}_i - \underline{r}_j|} - e^2 \sum_i \sum_J \frac{Z_J}{|\underline{r}_i - \underline{R}_J|} \\
 & - \frac{i\hbar^2}{4m^2 c^2} \sum_i \underline{\sigma}_i \cdot \nabla V(\underline{r}_i) \times \nabla_i - \beta_e \sum_i \left(\underline{L}_i + g \frac{\underline{\sigma}_i}{2} \right) \cdot \underline{H}
 \end{aligned} \tag{5-1}$$

$$+ 2 \sum_J \gamma_J \beta_e \beta_n \sum_k \left\{ \frac{(\underline{L}_i - g/4 \underline{\sigma})}{|\underline{r}_i - \underline{R}_J|^3} \cdot \underline{I}_J + \right. \\ \left. + \frac{3}{4} g \frac{(\underline{r}_i - \underline{R}_J) \cdot \underline{\sigma} (\underline{r}_i - \underline{R}_J) \cdot \underline{I}_J}{|\underline{r}_i - \underline{R}_J|^5} + \frac{4\pi g}{3} \delta(\underline{r}_i - \underline{R}_J) \underline{\sigma} \cdot \underline{I}_J \right\}$$

where $\beta_e = \frac{e\hbar}{2mc}$, the Bohr magneton
 $\beta_n = \frac{e\hbar}{2Mc}$, the nuclear magneton
 g is the electronic g factor
 γ is the nuclear g factor.

The symbols e , m , M , $\hbar$ and ∇ have their usual meanings and $V(\underline{r}_i)$ is the potential energy of an electron at position $\underline{r}_i$. $\underline{I}_J$ is the spin operator for the J^{th} nucleus at $\underline{R}_J$ and $\underline{\sigma}_i$ and $\underline{L}_i$ the spin and angular momentum operators for the electron with coordinate $\underline{r}_i$, $i=1,2,\dots,\sum_J Z_J$.

Here the first term in (5-1) is the kinetic energy of the electrons, the second, third and fourth terms account for the electrostatic interaction of the electrons and nuclei²⁵ and the fifth term is the spin-orbit interaction.²⁶ The sixth is the interaction with an external magnetic field and the seventh is the hyperfine interaction of the electrons and nuclei.²⁷

The interaction of the electron with the $\underline{H}$ field is taken only to the first order in $\underline{H}$ since the quadratic terms are small for the fields involved and only

give rise to a diamagnetic effect which is not of interest in the present calculation. The interactions of the nuclear dipoles with the magnetic field are also ignored since they are at least three orders of magnitude less than the interaction of the electron spins with H .

The potential, $V(\underline{r})$, experienced by an electron is the sum of that due to the atom it is "on" plus the potentials due to neighboring atoms. To estimate the relative importance to the spin-orbit interaction of the fields of neighbors and the internal atomic field, we note that there is no spin-orbit effect in the hydrogen and that the 3p electron of argon will experience the greatest effect of the crystal field. For two argon atoms at normal lattice spacing the contribution of one's potential relative to the internal field of the other atom evaluated at point r on the line joining the nuclei is just the ratio $\left. \frac{\partial V(r)}{\partial r} \right|_{z,1-r} : \left. \frac{\partial V(r)}{\partial r} \right|_r$. Since the 3p electron spends most of its time inside $r = 2a_0$, the maximum of the probability function occurring near $1.3a_0$, a good measure of the relative importance of these two terms is the ratio for $r = a_0$. At this point we have $1:10^5$ indicating that we need only consider the spherically symmetric internal atomic potential in spin-orbit calculations.²⁸ In this case the spin-orbit operator reduces to

$$\frac{\hbar^2}{4m^2c^2} \cdot \frac{1}{r} \frac{\partial V(r)}{\partial r} \underline{L} \cdot \underline{\sigma}$$

The Hamiltonian is clearly the sum of the operators for the internal atomic interactions plus the interactions between the atoms in the crystal. For the case of the A:H system, the order of magnitude of the terms may be estimated as follows:

1. The hydrogen binding energy is 13.6 ev and the argon binding energies are equal to or greater than the ionization energy of the 3p electron which is 15.8 ev.

2. Estimates of the Van der Waals interaction between various atoms are given in Table III.*

TABLE III. The Van der Waals Interaction between Argon and Hydrogen Atoms

Atoms	Spacing	E_{VdW} ev/bond
A - A	In normal lattice - $7.1a_0$	-0.013
A - H	" " " "	-0.005
A - H	In cramped site - $4a_0$	-0.2

* The argon-argon interaction may be estimated from the heat of sublimation of solid argon. This is 1.77 kcal/mol²⁹ or 0.08 ev/atom and arises mainly from interaction with an argon atom's twelve nearest neighbors. Hence the energy per bond is $2 \times (0.08/12)$

~ 0.013 ev/bond.

An independent check on the argon-argon interaction can be made using the Kirkwood-Buckingham formula that gives the dipole-dipole interaction in terms of the atomic polarizabilities, α . In atomic units the relation is³⁰

$$E_{vdw} = -\frac{2}{3} \cdot \frac{1}{R^6} \cdot \frac{\alpha_1 \alpha_2}{\sqrt{\frac{\alpha_1}{N_1}} + \sqrt{\frac{\alpha_2}{N_2}}}$$

where R is the internuclear distance and N_1 and N_2 the number of electrons in atoms 1 and 2. The polarizability of argon is $1.63 \times 10^{-24} \text{ cm}^3$ ³¹ and at the normal lattice spacing of $7.1a_0$ the Van der Waals energy is approximately 2×10^{-2} ev/bond.

The hydrogen-argon interaction may be estimated using the polarizability of hydrogen, $0.667 \times 10^{-24} \text{ cm}^3$.³²

The result is

$$E_{vdw}(A:H) \sim \frac{15 \times 10^{-48}}{R^6} \text{ ev cm}^6$$

3. An estimate of the crystal field interaction is given by the first-order energy of the hydrogen 1s state in the self-consistent field of an argon atom. Values for the matrix element $(\varphi^{1s} | V(\underline{r}) | \varphi^{1s})$ where φ^{1s} is the atomic 1s state of hydrogen and $V(\underline{r})$ is Hartree's

self-consistent potential for argon with exchange³³, are given in Table IV.

TABLE IV. Matrix Elements of the Atomic Argon Potential

A-H internuclear distance	$(\psi^{1s} V(r)_{\text{Argon}} \psi^{1s})$ in ev
4 a_0	-0.372
5 a_0	-0.0604
6.5 a_0	-0.00348
8 a_0	-0.00018

4. In the solid, overlap of the hydrogen-atom wave function with argon p functions leads to an effective mixing of hydrogen 1s states and argon p states of the same spin as the hydrogen atom's electron. Thus there exists a part of the crystal wave function made up of a linear combination of p functions that has unpaired spin. It is of order S^2 and the spin is the same as that of the paramagnetic electron.

$S_{A3p, H1s}$ is of order 0.1 to 0.001 and the zero-order spin-orbit matrix element for the 3p state may be estimated from the work of Knox who calculated the spin-orbit interaction for the 3p term of the excited argon configuration ($3p^5 4s$). The excited 3p wave function differs from the unexcited function only by being

slightly more compressed and the spin-orbit interaction calculated from them is good enough to give an order of magnitude. Knox³⁴ found that the spin-orbit interaction was approximately 0.12 ev. This coupled with the factor of S^2 leads to interactions for the unpaired p-like component of the impurity wave function of less than 0.01 ev for even the most cramped trapping sites.

5. The net angular momentum of the closed-shell rare-gas atoms is zero, hence the interaction of the system with an external magnetic field is essentially the dipole energy of the unpaired electron spin of the hydrogen's electron. For fields of the order of 3000 gauss, this amounts to energies of magnitude 10^{-5} ev.

6. Since the isotopes of argon, A^{18} , A^{20} and A^{22} , all have zero nuclear spin, the only contribution to the hyperfine interaction will be from the proton of the hydrogen. In the free atom, this amounts to a splitting of 1430.4 mc/sec, or 6×10^{-6} ev.

From these estimates of the various terms in the energy we see three well defined 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 H field and the hyperfine interaction of order 10^{-5} ev.

From this division of the Hamiltonian, we have a straightforward procedure for calculating the expectation values of the interactions in group III. We start with wave functions that are solutions to the atomic problem, then correct them for the Van der Waals, crystal field, and spin-orbit interactions to form a wave function for the crystal. The interactions in group III are then treated as perturbations on the crystal energy.

In addition to the above picture of the shifts of the hyperfine splitting, an additional effect exists. Bender^{35,36} has pointed out that the hyperfine interaction produces changes in the multipole moments of the hydrogen ground state. This change is different for the two hyperfine states of the impurity and so the Van der Waals interaction which depends on the multipole moments will differ from one state to the other. This difference in interaction can be considered as an additional shift in the hyperfine splitting.

Physically this can be seen for hydrogen as follows. There are two hyperfine states, one with the electronic and nuclear spins parallel and one with them

antiparallel. The Fermi term of the hyperfine interaction admixes higher s states to the ground state and in one case these more diffuse states are added and in the other they are subtracted. As a first approximation, the multipole moments for these two states will be increased and decreased respectively. The Van der Waals interaction will therefore differ for the two states and this difference will be proportional to $\underline{I} \cdot \underline{\sigma}$. In the spin Hamiltonian formalism, this term is lumped in with the hyperfine interaction.

For simplicity we have ignored this effect in developing the present theory since the operators involved are formally the same as the crystal field and the spin-orbit operators. In a numerical calculation this effect can be included by the same techniques as developed here or the perturbation theory results of Herman and Margenau³⁶ may be used.

CHAPTER VI

THE CRYSTAL WAVE FUNCTION

In the absence of interactions between atoms, the wave function for the system in the one-electron approximation is an antisymmetrized product of one-electron functions

$$A \Phi_0, \quad (6-1)$$

where A is the usual antisymmetrization operator

$$\frac{1}{\sqrt{N!}} \sum_{\nu=1}^{N!} (-1)^{P_\nu} P_\nu, \quad \text{and } \Phi_0 \text{ is the product of the}$$

one-electron functions, $\phi^{\xi}(\underline{r}_i)$, occupied by the N electrons of the system, $\prod_{\xi} \phi^{\xi}(\underline{r}_i)$.

In order to modify this to take account of interactions in the crystal, we use the variational method,^{*} relying in part on a procedure due to Hassé.^{37,38} In this, one adds to the wave function a correction that is

^{*} Since this work was begun, W. Marshall and R. Stuart³⁹ in a discussion of transition ion complexes outlined an identical approach to the problem of a tight binding paramagnetic center. They suggest that one should "choose individual atomic-like wave functions for the electrons of the magnetic ion and of the ligands and let these wave functions be specified by as many variational parameters as seem necessary. Assuming the crystal to be described by a Heitler-London model, now calculate the total energy of the crystal (working to second order, say, in the overlap integrals) and minimize this total energy by varying the parameters."

proportional to both the initial wave function and the perturbation. For example, consider the Hamiltonian

$$H = H_0 + \hbar \quad (6-2)$$

for which $\hbar$ is a perturbation on H_0 . Assume H_0 has a ground state eigenfunction ψ_0 . Then, Hassé's method is to seek a solution of the eigenvalue problem of the form

$$\psi = \psi_0 (1 + \lambda \hbar). \quad (6-3)$$

The variational parameter λ is found by minimizing the expectation value of H . The approximate solution is:

$$\begin{aligned} \lambda = & \quad (6-4) \\ = & \frac{\langle \psi_0 | H_0 | \hbar \psi_0 \rangle - \langle \psi_0 | H | \psi_0 \rangle \langle \psi_0 | \hbar | \psi_0 \rangle}{\langle \hbar \psi_0 | H | \hbar \psi_0 \rangle - \langle \psi_0 | H | \psi_0 \rangle \langle \hbar \psi_0 | \hbar \psi_0 \rangle - 4 \langle \psi_0 | \hbar | \psi_0 \rangle} \\ & [\langle \psi_0 | H | \hbar \psi_0 \rangle - \langle \psi_0 | H | \psi_0 \rangle \langle \psi_0 | \hbar | \psi_0 \rangle] \end{aligned}$$

This should be compared with the first-order perturbation theory correction to the wave function. Here $\hbar \psi_0 = \psi_1$ corresponds to the "excited state" being admixed, and if ψ_0 and ψ_1 were orthogonal and ψ_1 normalized, the expression for λ would take on the more familiar form

$$\lambda = \frac{\langle \psi_0 | \mathcal{H} | \psi_1 \rangle}{E_1 - E_0} . \quad (6-5)$$

where E_0 and E_1 are the energies of states ψ_0 and ψ_1 respectively.^{40,41}

Hassé applied this method to find atomic polarizabilities and, in the case of hydrogen, it gave about 12% accuracy with just this one additional term.³⁷ Later this method was used by Hassé³⁸, Slater and Kirkwood⁴² and Buckingham⁴³ to calculate Van der Waals interactions and by Kojima⁴⁴ to treat spin-orbit interactions in F centers.

To apply this method to the present problem, we write the modified crystal wave function as

$$\Phi = \alpha \left[1 + \sum_{\xi} \mathcal{E}^{\xi}(\underline{r}_{\xi}) + \sum_{\xi} \mathcal{H}^{\xi}(\underline{r}_{\xi}) + \sum_{\xi} \sum_{\eta} \mathcal{D}^{\xi\eta}(\underline{r}_{\xi}, \underline{r}_{\eta}) \right] \Phi_0 \quad (6-6)$$

where

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

$$\mathcal{H}^{\xi}(\underline{r}_{\xi}) = \mathcal{L}^{\xi} \omega^{\xi}(\underline{r}_{\xi}) \underline{L} \cdot \underline{\sigma}$$

and

$$\mathcal{D}^{\xi\eta}(\underline{r}_{\xi}, \underline{r}_{\eta}) = \lambda^{\xi\eta} u^{\xi\eta}(\underline{r}_{\xi}, \underline{r}_{\eta}) .$$

Here Λ^{ξ} , $\mathcal{L}^{\xi}$ and $\lambda^{\xi\eta}$ are variational parameters and $v^{\xi}(\underline{r}_{\xi})$, $\omega^{\xi}(\underline{r}_{\xi})$ and $u^{\xi\eta}(\underline{r}_{\xi}, \underline{r}_{\eta})$ are functions of $\underline{r}_{\xi}$ and $\underline{r}_{\eta}$ as shown.

We intend that the wave function ϕ^3 is to be corrected by $v^3(r_3)$ for crystal field effects and by $\omega^3(r_3) \underline{L} \cdot \underline{\sigma}$ for spin-orbit effects. The last term $u^{37}(r_3, r_7)$ corrects the product of the wave functions ϕ^3 and ϕ^7 simultaneously for the Van der Waals effect.* This "simultaneous" correction is necessary since the Van der Waals force arises from a correlation of the motion of electrons on adjacent atoms. Here we limit ourselves to the two-electron correlation part of the many-body problem as is the usual practice.^{45,46,47} We note that the use of $u^{37}(r_3, r_7)$ in the variational approach corresponds to the use of the product of

* For example, in the two-electron case $\Phi_0 = \phi^1(r_1) \phi^2(r_2)$ and Φ , the corrected wave function, is

$$\begin{aligned} \Phi &= [1 + \mathcal{E}^1(r_1) + \mathcal{E}^2(r_2) + \mathcal{H}^1(r_1) + \mathcal{H}^2(r_2) + \\ &\quad + \mathcal{Y}^{1,2}(r_1, r_2)] \Phi_0 \\ &= \phi^1(r_1) \phi^2(r_2) \\ &\quad + \{ [\mathcal{E}^1(r_1) + \mathcal{H}^1(r_1)] \phi^1(r_1) \} \phi^2(r_2) \\ &\quad + \phi^1(r_1) \{ [\mathcal{E}^2(r_2) + \mathcal{H}^2(r_2)] \phi^2(r_2) \} \\ &\quad + \mathcal{Y}^{1,2}(r_1, r_2) \phi^1(r_1) \phi^2(r_2). \end{aligned}$$

Here the second and third terms show how the individual functions are corrected. The fourth term shows the simultaneous correction.

two excited-state functions for this correction in perturbation theory.⁴⁵

If we were to follow Hassé's method strictly, we should replace $\psi(\underline{r})$ and $\omega(\underline{r}) \underline{L} \cdot \underline{\sigma}$ by $V(\underline{r})$, the crystal field potential, and $(\hbar^2/4m^2c^2) \frac{\partial V(\underline{r})}{\partial r} \underline{L} \cdot \underline{\sigma}$, the spin-orbit interaction, respectively. However, $V(\underline{r})$ is singular at the nuclei and leads to divergencies in the matrix elements. We consequently seek better-behaved variational functions. Reasonable choices would be the perturbation times some cutoff function or a modification of the wave function similar to the use of a screening factor.

An example of the latter is the simple variational treatment of the helium atom in which the wave function e^{-Zr} is used.⁴⁸ Here Z is a variational parameter representing the "effective" charge on the nuclei. Other ways of looking at Z are to consider it a screening parameter or a change-in-scale factor of the wave function's unit of length. In the case of an impurity in a highly symmetric site we might expect that the crystal field would cause a spreading-out of the electronic charge cloud corresponding to a decrease in the effective charge of the impurity nucleus that would be primarily spherically symmetric.

Provided this effect were small, the ground-state wave function of the hydrogen impurity, ϕ^{1s} , could be modified for crystal field effects by forming the corrected wave function, $\phi^{1s'}$, as follows:

$$\begin{aligned}\phi^{1s'} &= e^{-(1-\delta)r} = \phi^{1s} e^{\delta r} \\ &\approx \phi^{1s} \left(1 + \delta r + \frac{\delta^2 r^2}{2} + \dots\right)\end{aligned}\tag{6-7}$$

where δ is the change from $Z = 1$ introduced by the crystal field. Keeping the two leading terms we might then seek a modification of the hydrogen 1s function of the form

$$\phi^{1s} \rightarrow \phi^{1s} (1 + \delta r).\tag{6-8}$$

In fact this can be generalized to gain a second degree of freedom by seeking a wave function of the form

$$\phi^{1s'} = \phi^{1s} (1 + \delta r^n)\tag{6-9}$$

where both δ and n are to be chosen to minimize the energy.⁴²

Because of the simplicity of this form for actual computations we shall use it as a modification of Hassé's approach for both the crystal field and spin-orbit corrections. These specific functions will be introduced late in the calculations, however, so an extension of the work could easily be made with some other choice.

For $u^{3\gamma}(\underline{r}_\xi, \underline{r}_\eta)$ we will use the first term of the multipole expansion for the Van der Waals interaction.⁴⁹ This is the familiar dipole-dipole term given by

$$u^{3\gamma}(\underline{r}_\xi, \underline{r}_\eta) = e^2 \frac{(\underline{r}_\xi - \underline{R}_\xi) \cdot (\underline{r}_\eta - \underline{R}_\eta) - 3(\underline{r}_\xi - \underline{R}_\xi) \cdot \hat{\underline{R}} (\underline{r}_\eta - \underline{R}_\eta) \cdot \hat{\underline{R}}}{R^3} \quad (6-10)$$

$\underline{R}_\xi$ and $\underline{R}_\eta$ are respectively the coordinates of the nuclei on which $\phi^\xi(\underline{r}_\xi)$ and $\phi^\eta(\underline{r}_\eta)$ are centered, $\underline{R} = \underline{R}_\xi - \underline{R}_\eta$ is the separation of the nuclei and $\underline{r}_\xi$ and $\underline{r}_\eta$ are the coordinates of the electrons. Here we limit the discussion to interatomic correlation, setting

$$u^{3\gamma}(\underline{r}_\xi, \underline{r}_\eta) = 0 \quad (6-11)$$

if $\phi^\xi(\underline{r}_\xi)$ and $\phi^\eta(\underline{r}_\eta)$ are centered on the same nucleus. This separation of correlation in the many-body problem into correlation between groups of electrons is discussed in detail by Sinanoglu.⁴⁷

Since our main concern is with the paramagnetic atom, i.e., hydrogen, not all the variational parameters will be equally important in calculating the paramagnetic effects. In particular we find in Chapter VII that we must calculate λ 's for all hydrogen-argon interactions, $\mathcal{L}$ for both hydrogen and argon spin-orbit effects, but Λ only for the hydrogen atom.

In order to simplify the calculation of the crystal energy, we will use orthonormalized one-electron functions to form Φ_0 . We choose Löwdin's method of symmetric orthonormalization⁵⁰ to transform the basic set of atomic wave functions. A summary of Löwdin's procedures and comments on the convergence of the resulting series are given in Appendix B.

CHAPTER VII

CALCULATION OF THE VARIATIONAL PARAMETERS

1. The Crystal Energy

In order to make the solution for the variational parameters tractable, we must make several simplifying assumptions. First we shall assume that an impurity atom interacts only with the material in which it is trapped and not with other impurity atoms. This is reasonable because for the small concentration of impurities used in experiments the impurity atoms should be well separated. Furthermore, we assume that argon continues to crystallize in a face-centered cubic structure when small amounts of impurities are present. Thus the impurity will be trapped in one of the three possible sites discussed in Chapter IV. The lattice may relax some about the trapped atom, but we assume that any relaxation is symmetric, all of the neighbors moving by the same amount, but preserving the symmetry of the trapping site.⁵¹

The estimates of the total next-nearest-neighbor interactions relative to those of the nearest neighbors, given in Chapter IV, indicate that we need only consider the neighbors nearest the impurity in calculating its interactions with the lattice. For purposes of finding

the parameters associated with the impurity we shall therefore limit our "crystal" to the impurity and its nearest neighbors. In later calculations, for example, in calculating the relaxation by the configuration coordinate method, it may be necessary to consider the interactions among the nearest neighbor atoms and between this group and the rest of the crystal. This can be done by using either phenomenological interaction potentials such as the Lennard-Jones 6-12 potential^{52,53} or theoretical estimates.⁵⁴

In calculating the wave function for the impurity in this system, we shall attempt to find the parameters correct to order " S^2 ", that is, to the square of the maximum overlap integral between the wave functions of the impurity and those of the atoms of the host lattice.

Since our main concern is with the hydrogen impurity, we shall calculate the crystal field parameter, Λ^ξ , only for this atom, so, $\xi = 0$ where 0 represents the hydrogen 1s function. As will become clear in the calculations, the Λ 's for molecular crystals vary much like the square of the overlap integral. The effect of Λ 's for one atom on the wave functions of a neighboring atom arises largely from orthogonalization of their wave functions. The resulting correction to a neigh-

bor's wave function is proportional to $\Lambda^{\eta} \langle \phi^{\xi} | v^{\eta} | \phi^{\eta} \rangle$ where ϕ^{ξ} is the wave function of the neighbor and ϕ^{η} is the wave function of the first atom. Since Λ^{η} is of order S^2 to start with, the correction to the wave function of the impurity for Λ 's of its neighbors is of order S^3 and so negligible in our approximation.

In calculating the Van der Waals parameters we shall encounter matrix elements of the form

$$\lambda^{\xi\eta} \lambda^{\nu\mu} (\xi_i \eta_j | u_{ij}^{\xi\eta} u_{ij}^{\nu\mu} | \nu_i \mu_j)$$

where neither ν nor μ is equal to either ξ or η . While for ξ and ν on different atoms and η and μ on different atoms, this term may be of order S^2 , it represents the Van der Waals or electrostatic correlation interaction among four different electrons. Similarly $\lambda^{\xi\eta} \lambda^{\xi\mu} (\xi_i \eta_j | u_{ij}^{\xi\eta} u_{ij}^{\xi\mu} | \xi_i \mu_j)$ for $\mu \neq \eta$ represents the interaction among three different electrons. From the work of Axilrod and Teller⁴⁶ we know that the triple dipole interaction represents only 2 to 9% of the total cohesive energy in rare gases, so we shall neglect the three-electron and also the four-electron correlations. That is, we shall keep matrix elements arising from the Van der Waals correction only if they have the form $\langle \xi_i \eta_j | u_{ij}^{\xi\eta} u_{ij}^{\xi\eta} | \xi_i \eta_j \rangle$ or $\langle \xi_i \eta_j | u_{ij}^{\xi\eta} u_{ij}^{\eta\xi} | \eta_i \xi_j \rangle$. As mentioned before, we

shall also neglect correlation terms within atoms by setting $u_{ij}^{\xi\eta} = 0$ if ϕ^{ξ} and ϕ^{η} are centered on the same atom. Again, since we are most interested in the impurity, we shall calculate $\lambda^{\xi\eta}$ only for either ξ or η an impurity function. For the A:H system we will therefore only solve for $\lambda^{o,p}$ and $\lambda^{p,o}$ where ϕ^p is an argon wave function and ϕ^o is the hydrogen 1s state.

Another simplification is introduced by the fact that $\mathcal{L}^{\xi}$, the spin-orbit splitting parameter for the argon atoms, occurs only in the magnetic properties of the impurity with coefficients proportional to S^2 . Hence $\mathcal{L}^{\xi}$ is needed only to order S^0 to compute observable paramagnetic effects to order S^2 .

Our final assumption is that we may neglect overlap integrals between the host crystal atoms neighboring the impurity. The main role of overlap in the host crystal is to provide the repulsive forces between atoms and so determine the lattice for the pure crystal. For our purposes we shall take this as a given geometry and work from there. Beyond this, the host-host overlap would only enter the impurity wave function by way of the host-impurity orthogonalization subtracting from the impurity wave function a host atom's wave function that is orthogonalized to the wave function of another

host atom.

To apply the variational method to find the parameters we must first find the expectation value of the crystal energy ignoring the hyperfine and magnetic field interactions. That is, we seek

$$E = \frac{\langle \Phi | \mathcal{H}' | \Phi \rangle}{\langle \Phi | \Phi \rangle} \quad (7-1)$$

in terms of the parameters Λ^3 , $\mathcal{L}^3$ and $\lambda^3 \eta$. Here $\mathcal{H}'$ comprises the first five terms of the complete Hamiltonian, Eq. (5-1), and Φ is the crystal wave function, Eq. (6-6).

To avoid the unreasonable complication of writing this in terms of atomic functions at this point, we shall use an abbreviated form for the matrix element and then minimize the resulting expression. First we expand the wave function:

$$\begin{aligned} \Phi &= a \Phi_0 + a \sum_{\xi} \mathcal{E}_{(\underline{r}_{\xi})}^3 \Phi_0 + a \sum_{\xi} \mathcal{H}_{(\underline{r}_{\xi})}^3 \Phi_0 \\ &\quad + a \sum_{\xi} \sum_{\eta} \mathcal{H}_{(\underline{r}_{\xi}, \underline{r}_{\eta})}^3 \eta \Phi_0 \\ &= u_0 + u_1 + u_2 + u_3 \end{aligned} \quad (7-2)$$

where we identify u_0 with $a \Phi_0$, u_1 with $a \sum_{\xi} \mathcal{E}_{(\underline{r}_{\xi})}^3 \Phi_0$ and so on. Then in the "u" notation the energy is:

$$\begin{aligned}
& \langle u_0 | \mathcal{H}' | u_0 \rangle + [\langle u_1 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_1 \rangle] + \langle u_1 | \mathcal{H}' | u_1 \rangle \\
& + [\langle u_2 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_2 \rangle] + \langle u_2 | \mathcal{H}' | u_2 \rangle \\
& + [\langle u_3 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_3 \rangle] + \langle u_3 | \mathcal{H}' | u_3 \rangle \\
& + \langle u_1 | \mathcal{H}' | u_2 \rangle + \langle u_2 | \mathcal{H}' | u_1 \rangle \\
& + \langle u_1 | \mathcal{H}' | u_3 \rangle + \langle u_3 | \mathcal{H}' | u_1 \rangle \\
& + \langle u_2 | \mathcal{H}' | u_3 \rangle + \langle u_3 | \mathcal{H}' | u_2 \rangle \\
E = & \frac{\quad}{1 + 2 \langle u_1 | u_0 \rangle + \langle u_1 | u_1 \rangle + 2 \langle u_2 | u_0 \rangle + \langle u_2 | u_2 \rangle + 2 \langle u_3 | u_0 \rangle + \langle u_3 | u_3 \rangle} \\
& + \langle u_1 | u_2 \rangle + \langle u_2 | u_1 \rangle \\
& + \langle u_1 | u_3 \rangle + \langle u_3 | u_1 \rangle \\
& + \langle u_2 | u_3 \rangle + \langle u_3 | u_2 \rangle \quad (7-3)
\end{aligned}$$

If the tight binding approximation is to hold, we expect that the correction to the normalization appearing in the denominator is very small compared to unity; hence we shall expand the denominator in a binomial series keeping up to the second power in the correction. Thus for $\mathcal{X}$ equal to the normalization correction we have:

$$\frac{1}{1+\mathcal{X}} \approx 1 - \mathcal{X} + \mathcal{X}^2.$$

The result of multiplying the expansion for the denominator times the numerator and keeping terms up to the square of the variational parameters gives

$$\begin{aligned}
E = E &+ \left\{ [\mu - \epsilon \alpha]_{\Lambda} + [(\nu - \epsilon \beta) - \alpha(\mu - \epsilon \alpha)]_{\Lambda^2} \right\} \\
&+ \left\{ [M - \epsilon A]_{\mathcal{L}} + [(N - \epsilon B) - A(M - \epsilon A)]_{\mathcal{L}^2} \right\} \\
&+ \left\{ [m - \epsilon a]_{\lambda} + [(n - \epsilon b) - a(m - \epsilon a)]_{\lambda^2} \right\} \\
&+ \left\{ P_{\Lambda \mathcal{L}} - \epsilon C_{\Lambda \mathcal{L}} - (\alpha M + A \mu) + 2 \epsilon \alpha A \right\}_{\Lambda \mathcal{L}} \\
&+ \left\{ P_{\Lambda \lambda} - \epsilon C_{\Lambda \lambda} - (\alpha m + a \mu) + 2 \epsilon \alpha a \right\}_{\Lambda \lambda} \\
&+ \left\{ P_{\mathcal{L} \lambda} - \epsilon C_{\mathcal{L} \lambda} - (a m + A m) + 2 \epsilon a A \right\}_{\mathcal{L} \lambda}
\end{aligned}
\tag{7-4}$$

where we have used the abbreviations

$$\begin{aligned}
\epsilon &= \langle u_0 | \mathcal{H}' | u_0 \rangle \\
\alpha &= 2 \langle u_1 | u_0 \rangle & \mu &= \langle u_1 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_1 \rangle \\
A &= 2 \langle u_2 | u_0 \rangle & M &= \langle u_2 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_2 \rangle \\
a &= 2 \langle u_3 | u_0 \rangle & m &= \langle u_3 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_3 \rangle \\
\beta &= \langle u_1 | u_1 \rangle & \nu &= \langle u_1 | \mathcal{H}' | u_1 \rangle \\
B &= \langle u_2 | u_2 \rangle & N &= \langle u_2 | \mathcal{H}' | u_2 \rangle \\
b &= \langle u_3 | u_3 \rangle & n &= \langle u_3 | \mathcal{H}' | u_3 \rangle
\end{aligned}
\tag{7-5}$$

$$\begin{aligned}
C_{\Lambda \mathcal{L}} &= \langle u_1 | u_2 \rangle + \langle u_2 | u_1 \rangle & P_{\Lambda \mathcal{L}} &= \langle u_1 | \mathcal{H}' | u_2 \rangle + \langle u_2 | \mathcal{H}' | u_1 \rangle \\
C_{\Lambda \lambda} &= \langle u_1 | u_3 \rangle + \langle u_3 | u_1 \rangle & P_{\Lambda \lambda} &= \langle u_1 | \mathcal{H}' | u_3 \rangle + \langle u_3 | \mathcal{H}' | u_1 \rangle \\
C_{\mathcal{L} \lambda} &= \langle u_2 | u_3 \rangle + \langle u_3 | u_2 \rangle & P_{\mathcal{L} \lambda} &= \langle u_2 | \mathcal{H}' | u_3 \rangle + \langle u_3 | \mathcal{H}' | u_2 \rangle
\end{aligned}$$

In words this simply says that the crystal energy is the energy calculated with uncorrected wave functions, ϵ , plus the energy associated with the variational terms. In the approximation we are using, this additional energy is the sum of nine terms: that due to Λ^3 and Λ^{ξ^2} , $\mathcal{L}^3$ and $\mathcal{L}^{\xi^2}$, $\lambda^{\xi\eta}$ and $\lambda^{\xi\eta^2}$ and the cross terms $\Lambda^3\mathcal{L}^{\eta}$, $\Lambda^3\lambda^{\eta\rho}$ and $\mathcal{L}^{\xi}\lambda^{\eta\rho}$. We have grouped the contributions together, each square bracket enclosing one of the nine terms. They appear in Eq. (7-4) in the same order as mentioned above, the brackets being labeled with a subscript to indicate the term.

To make the form of the equation somewhat clearer, let us write the Hamiltonian in the general form

$$\mathcal{H}' = W + \sum_i H_i + \sum'_{ij} G_{ij} \quad (7-6)$$

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

In terms of these quantities, ϵ is

$$\begin{aligned}
\epsilon = & W + \sum_{\xi} \langle \phi^{\xi}(x_i) | H_i | \phi^{\xi}(x_i) \rangle \\
& + \sum_{\xi} \sum_{\eta \neq \xi} \langle \phi^{\xi}(x_i) \phi^{\eta}(x_j) | G_{ij} | \phi^{\xi}(x_i) \phi^{\eta}(x_j) \rangle \\
& - \langle \phi^{\xi}(x_i) \phi^{\eta}(x_j) | G_{ij} | \phi^{\eta}(x_i) \phi^{\xi}(x_j) \rangle
\end{aligned}
\tag{7-7}$$

This is the sum of atomic binding energies plus the first-order perturbation-theory energy for the interactions within the solid. Löwdin used this term as the starting point for his calculation of the cohesive energy of ionic crystals⁵⁵ and Bleich and Mayer⁵⁶ studied it in deriving the mutual repulsive energy of closed shell structures. In both these cases, the spin-orbit term was not considered since it does not contribute for closed shells.

To gain a feeling for the variational corrections let us look at the direct terms in Λ^{ξ} and Λ^{ξ^2} and the cross term in $\Lambda^{\xi\eta}$. Exchange terms are also present, but the direct terms are representative of the form of the energy. The direct term may be written as *

* Note: In the second line of (7-8) we introduce the rounded-bracket notation $(\phi | O_p | \phi)$ 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 $\langle \phi^{\xi} | O_p | \phi^{\xi} \rangle$. For simplicity of notation we shall generally abbreviate wave functions with their quantum number index and indicate their associated coordinate by a subscript. Thus $(\phi^{\xi}(x) |$ will be denoted $(\xi |$.

$$\begin{aligned}
\mu - \epsilon \alpha &= 2 [\langle u_1 | \mathcal{H}' | u_0 \rangle - \langle u_1 | u_0 \rangle \langle u_0 | \mathcal{H}' | u_0 \rangle] \\
&= 2 \sum_{\xi} \left\{ (\varphi^{\xi} | v^{\xi} \sum' V_{\xi} | \varphi^{\xi}) - \right. \\
&\quad \left. - (\varphi^{\xi} | v^{\xi} | \varphi^{\xi}) (\varphi^{\xi} | \sum' V_{\xi} | \varphi^{\xi}) \right\},
\end{aligned}
\tag{7-8}$$

where $\sum' V_{\xi}(r_i)$ is the sum of the potentials of all the atoms except the one on which φ^{ξ} is centered. It is the perturbing crystal field potential. The energy eigenvalue of φ^{ξ} cancels between the first and second terms leaving 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.

The " Λ^{ξ^2} " term is

$$\begin{aligned}
E_{\Lambda^2} &= [(v - \epsilon \beta) - \alpha(\mu - \epsilon \alpha)] \\
&= \langle u_1 | \mathcal{H}' | u_1 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_1 | u_1 \rangle \\
&\quad - 4 \langle u_1 | u_0 \rangle [\langle u_1 | \mathcal{H}' | u_0 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_1 | u_0 \rangle].
\end{aligned}
\tag{7-9}$$

When expanded and only direct terms are retained, this becomes

$$\begin{aligned}
E_{\Lambda^2} = \sum_{\xi} \Lambda^{\xi^2} \left\{ \frac{1}{2} (\xi | \underline{\nabla} v^{\xi} \cdot \underline{\nabla} v^{\xi} | \xi) \right. \\
+ (\xi | v^{\xi^2} \Sigma' V_{\xi} | \xi) - (\xi | v^{\xi^2} | \xi) (\xi | \Sigma' V_{\xi} | \xi) \\
- 4 (\xi | v^{\xi} | \xi) [(\xi | v^{\xi} \Sigma' V_{\xi} | \xi) - (\xi | v^{\xi} | \xi) (\xi | \Sigma' V_{\xi} | \xi)] \Big\} \\
+ \sum_{\xi} \sum_{\eta \neq \xi} \Lambda^{\xi} \Lambda^{\eta} \left\{ (\xi | v^{\xi} \Sigma'' V_{\xi} | \xi) (\eta | v^{\eta} | \eta) \right. \\
+ (\xi | v^{\xi} | \xi) (\eta | \Sigma'' V_{\eta} | \eta) \\
+ (\xi_i \eta_j | v_i^{\xi} \frac{1}{r_{ij}} v_j^{\eta} | \xi_i \eta_j) \quad (7-10) \\
- (\xi | v^{\xi} | \xi) (\eta | v^{\eta} | \eta) \cdot \\
\left. [(\xi | \Sigma' V_{\xi} | \xi) + (\eta | \Sigma' V_{\eta} | \eta) + (\xi | \frac{1}{r_{ij}} | \xi) (\eta | \frac{1}{r_{ij}} | \eta)] \right. \\
\left. - 4 (\xi | v^{\xi} | \xi) [(\eta | v^{\eta} \Sigma' V_{\eta} | \eta) - (\eta | v^{\eta} | \eta) (\eta | \Sigma' V_{\eta} | \eta)] \right\}.
\end{aligned}$$

Here the new symbol $\Sigma'' V_{\xi}(r_i)$ is $\Sigma' V_{\xi}(r_i) - (\xi | \frac{1}{r_{ij}} | \xi)$.

Except for the term involving the operator $\underline{\nabla}$, this has the same general form as the Λ^{ξ} term, that of the matrix element of the product of a correction and the perturbation less the product of the matrix elements.

The " $\underline{\nabla}$ " term arises from the kinetic energy operator in the Hamiltonian and is a measure of the additional kinetic energy introduced by the correction to the wave function.

The " $\Lambda^{\xi} \mathcal{L}^{\eta}$ " term is

$$E_{\Lambda\mathcal{L}} = P_{\Lambda\mathcal{L}} - \epsilon C_{\Lambda\mathcal{L}} - (\alpha M + A\mu) + 2\epsilon\alpha A \quad (7-11)$$

which, on keeping only direct terms, becomes

$$\begin{aligned} E_{\Lambda\mathcal{L}} = \sum_{\xi} \Lambda^{\xi} \mathcal{L}^{\xi} \Big\{ & \frac{1}{2} (\xi | \nabla v^{\xi} \cdot \nabla (\omega^{\xi} \underline{L} \cdot \underline{\sigma}) | \xi) \\ & + (\xi | v^{\xi} \omega^{\xi} \underline{L} \cdot \underline{\sigma} \Sigma' V_{\xi} | \xi) \\ & - (\xi | v^{\xi} \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) (\xi | \Sigma' V_{\xi} | \xi) \quad (7-12) \\ & - [(\xi | v^{\xi} | \xi) (\xi | \Sigma' V_{\xi} \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) \\ & + (\xi | v^{\xi} \Sigma' V_{\xi} | \xi) (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) \\ & - 2 (\xi | v^{\xi} | \xi) (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) (\xi | \Sigma' V_{\xi} | \xi)] \Big\}. \end{aligned}$$

Here again we have a kinetic energy contribution plus terms of the form "matrix element of the product less product of the matrix elements".

All the other terms will be generally of one of these three forms. Thus we have the energy as a polynomial of second degree in the variational parameters, the coefficients of the polynomial being given by expressions involving the matrix elements of the variational functions. This may be written as

$$\begin{aligned} E = \epsilon & + \sum_{\xi} 2 I_{\xi} \Lambda^{\xi} + \sum_{\xi} \sum_{\eta} J_{\xi\eta} \Lambda^{\xi} \Lambda^{\eta} + \\ & + \sum_{\xi} 2 i_{\xi} \mathcal{L}^{\xi} + \sum_{\xi} \sum_{\eta} j_{\xi\eta} \mathcal{L}^{\xi} \mathcal{L}^{\eta} + \end{aligned}$$

$$\begin{aligned}
& + \sum_{\xi} \sum_{\eta \neq \xi} 2 \pi_{\xi \eta} \lambda^{\xi \eta} + \sum_{\xi} \sum_{\eta \neq \xi} \sum_p \sum_{p' \neq p} \Gamma_{\xi \eta, p p'} \lambda^{\xi \eta} \lambda^{p p'} \\
& + \sum_{\xi} \sum_{\eta} 2 K_{\xi \eta} \lambda^{\xi} \mathcal{L}^{\eta} \\
& + \sum_{\xi} \sum_{\eta} \sum_{p \neq \eta} 2 L_{\xi, \eta p} \wedge^{\xi} \lambda^{\eta p} \\
& + \sum_{\xi} \sum_{\eta} \sum_{p \neq \eta} 2 M_{\xi, \eta p} \mathcal{L}^{\xi} \lambda^{\eta p}. \quad (7-13)
\end{aligned}$$

The coefficients Γ_{ξ} , etc., are given explicitly in Appendix C. Notice here that the assumption that only two-electron correlations will be considered means $\lambda^{p p'}$ must be either $\lambda^{\xi \eta}$ or $\lambda^{\eta \xi}$.

To find the variational parameters we minimize Eq. (7-13). This leads to a set of coupled equations. For example, in the case of minimization with respect to $\wedge^{\xi}$,

$$\begin{aligned}
& \wedge_{\min}^{\xi} = \\
& = - \frac{\Gamma_{\xi} + \sum_{\eta \neq \xi} \frac{1}{2} (J_{\xi \eta} + J_{\eta \xi}) \wedge^{\eta} + \sum_{\eta} K_{\xi \eta} \mathcal{L}^{\eta} + \sum_{\eta} \sum_{p \neq \eta} L_{\xi, \eta p} \lambda^{\eta p}}{J_{\xi \xi}}. \quad (7-14)
\end{aligned}$$

Providing the coupling terms are small, this can be solved by iteration. Then as a first approximation,

$$\wedge_{\xi} = - \frac{\Gamma_{\xi}}{J_{\xi \xi}}. \quad (7-15)$$

From the tight binding picture we expect that the

coupling terms in the equations for the variational parameters are of secondary importance compared with the leading terms. The leading terms, such as I_{ξ} in Eq. (7-15), 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 must be much less than the direct one.

On this basis, we shall calculate the cross terms to order S^0 only, while calculating the leading term to order S^2 when solving for the variational parameters of the impurity's wave function.

2. The Crystal Field Parameters

The solution of the variational calculation for the crystal field parameters is

$$\Lambda_{\xi}^{\eta} = - \frac{I_{\xi}^{\eta}}{J_{\xi}^{\eta}} - \frac{\sum_{\eta' \neq \eta} \frac{1}{2} (J_{\xi}^{\eta'} + J_{\eta'}^{\xi}) \Lambda_{\xi}^{\eta'} + \sum_{\eta' \neq \eta} \frac{K_{\xi}^{\eta'} \mathcal{L}^{\eta'}}{J_{\xi}^{\eta'}} + \frac{\sum_{\eta' \neq \eta} \sum_{\rho \neq \rho'} L_{\xi, \eta' \rho} (\lambda^{\eta' \rho} + \lambda^{\rho \eta'})}{J_{\xi}^{\eta}} \quad (7-16)$$

where we have separated the right side into a first approximation and a correction term arising from cross terms with other parameters.

In Section 1 of Appendix C the detailed calculations for the quantities in (7-16) are given. Here we shall present the results and discuss the origin of the terms.

I_ξ for $\xi = 0$, the hydrogen 1s function, is given to second order in overlap by

$$\begin{aligned}
 I_0 = & (0|v^0\tilde{\Sigma}'V_0|0) - \sum_{\eta} (0|v^0\eta)(\eta|\tilde{\Sigma}'V_0|0) \\
 & - \frac{1}{2} \sum_{\alpha} S_{0\alpha} \{ (0|v^0\tilde{\Sigma}'V_{\alpha}|\alpha) + (\alpha|v^0\tilde{\Sigma}'V_0|0) \\
 & \quad - (0|v^0|0)[(0|\tilde{\Sigma}'V_{\alpha}|\alpha) + 2(\alpha|\tilde{\Sigma}'V_0|0)] \} \\
 & - \frac{1}{2} \sum_{\alpha} S_{0\alpha} \sum_{\eta \neq 0} \left\{ (0|0|\frac{v^0}{r_{ij}}|0\eta) - (00|\frac{v^0}{r_{ij}}|\eta 0) \right. \\
 & \quad \left. - (0|v^0|0)[(00|\frac{1}{r_{ij}}|0\eta) - (00|\frac{1}{r_{ij}}|\eta 0)] \right\}, \quad (7-17)
 \end{aligned}$$

where the potential $\tilde{\Sigma}'V_{\xi}(\mathbf{r}_i)$ is shorthand for the "exchange" potential defined by

$$\begin{aligned}
 \tilde{\Sigma}'V_{\xi}(\mathbf{r}_i)|\varphi_i^{\xi}) = & e^2 \left[- \sum_j \frac{z_j}{|\mathbf{r}_i - \mathbf{R}_j|} |\varphi_i^{\xi}) \right. \\
 & \left. + \sum_{\eta \neq \xi}^* (\eta_j|\frac{1}{r_{ij}}|\eta_j)|\varphi_i^{\xi}) - (\eta_j|\frac{1}{r_{ij}}|\xi_j)|\varphi_i^{\eta}) \right] \quad (7-18)
 \end{aligned}$$

Here the energy eigenvalues for the atomic wave functions have canceled leaving matrix elements of potentials and the variational function v^{ξ} . If $\tilde{\Sigma}'V_0$ were replaced with $\Sigma'V_0$ the first line of (7-17) is just that given by considering the direct terms to order S^0 in the

Löwdin expansion.

Roughly we may think of I_ξ as being a measure of the lowering of the potential energy of the electron as it moves in the "corrected" part of the wave function given by $v^\xi \phi^\xi$.

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. In Appendix C a numerical example of this dependence of the potential matrix elements is given for the case of argon and hydrogen and it is shown that $(\phi^0 | \sum' V_{\text{Argon}} | \phi^0)$ where ϕ^0 is the hydrogen 1s function, is nearly proportional to the square of the hydrogen 1s-argon 3p overlap.

From this it is reasonable to expect the leading terms of I_ξ to be of order S^2 where $\xi = 0$, the hydrogen ground state, and $\sum' V$ is given by the potential of neutral argon atoms surrounding the impurity.

The exchange corrections to the potential are of order S^2 and arise from considering the interaction of the exchange charge clouds $\phi^\xi^* \phi^\eta$ and $\phi^\eta^* \phi^\xi$ where

ϕ^{ξ} is a hydrogen function and ϕ^{η} an argon function.

The other terms in (7-17) arise from the overlap terms in the Löwdin series.

Since I_{ξ} is of order S^2 we need $J_{\xi\xi}$ only to order S^0 to find Λ^{ξ} to order S^2 . The result is

$$J_{\xi\xi} = \frac{1}{2} (\xi | \nabla v^{\xi} \cdot \nabla v^{\xi} | \xi). \quad (7-19)$$

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 $v^{\xi} \phi^{\xi}$.

The minimization of the crystal energy corresponds to balancing the increase in potential energy measured by I_{ξ} against the kinetic energy measured by $J_{\xi\xi}$.

As pointed out in Section 1 of this chapter, the cross terms in the equation for Λ^{ξ} , (7-16), represent "second generation" effects and as such we consider them only to order S^0 in finding Λ^{ξ} to order S^2 . In this sense, the term $\frac{1}{2} \frac{(J_{\xi\eta} + J_{\eta\xi})}{J_{\xi\xi}} \Lambda^{\eta}$ is negligible since Λ^{η} is of order S^2 in molecular crystals. In fact, since the matrix elements $J_{\xi\eta}$, $\eta \neq \xi$ themselves involve the crystal potential, this term is of order S^4 for the case of the hydrogen impurity.

The cross term $K_{32}/J_{33} L^{\eta}$ is zero for the case of φ^3 , a hydrogen 1s function. The main reason is that the coefficient K_{32} involves matrix elements of the spin-orbit correction which is proportional to $\underline{L} \cdot \underline{\sigma}$ and so gives zero for s states.

The cross term with the Van der Waals parameter, $L_{32} \eta \rho (\lambda^{\eta \rho} + \lambda^{\rho \eta})$, is given by

$$\begin{aligned} \sum_{\eta < \rho} L_{32} \eta \rho (\lambda^{\eta \rho} + \lambda^{\rho \eta}) &= \\ &= \sum_{\xi < \rho} (\lambda^{\xi \rho} + \lambda^{\rho \xi}) \left\{ (\xi, \rho | u_{ij}^{\xi \rho} v_{ij}^{\xi} | \xi, \rho) \right. \\ &\quad \left. (\xi, \rho | u_{ij}^{\xi \rho} v_{ij}^{\xi} | \xi, \rho) (\xi | v^{\xi} | \xi) \right. \\ &\quad \left. - \sum_{\eta < \rho} (\lambda^{\eta \rho} + \lambda^{\rho \eta}) (\eta, \rho | u_{ij}^{\eta \rho} v_{ij}^{\eta} | \eta, \rho) (\xi | v^{\xi} | \xi) \right\}. \end{aligned} \tag{7-20}$$

The first half of this contribution arises from the interaction of $u_{ij}^{\xi \eta}$ 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 $\phi^{\xi} + \sum \lambda^{\xi} v^{\xi} \phi^{\xi}$ exceeds its normalized value.

3. The Spin-Orbit Parameters

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

$$\mathcal{L}^{\xi} = -\frac{i\xi}{j_{\xi\xi}} - \quad (7-21)$$

$$-\frac{\sum_{\eta \neq \xi} \frac{1}{2}(j_{\xi\xi}^{\eta} + j_{\eta\xi}^{\eta})\mathcal{L}^{\eta} + \sum_{\eta} \frac{K_{\eta\xi}}{j_{\xi\xi}^{\eta}} \Lambda^{\eta} + \sum_{\eta < \rho} \sum_{\xi} M_{\xi\eta\rho}(\lambda^{\eta\rho} + \lambda^{\rho\eta})}{j_{\xi\xi}^{\eta}}.$$

In Chapter VIII it is shown that the spin-orbit parameters enter only the g-shift calculations and that they always appear with a coefficient proportional to S^2 . Thus we need find $\mathcal{L}^{\xi}$ only to order S^0 . This even holds for finding the wave function of an s-state impurity function to order S^2 . Here the $\mathcal{L}^{\xi}$ associated with the impurity will be that of the state admixed by orthogonalization. Since the amount of admixed state is proportional to S and the series for $\mathcal{L}^{\xi}$ has only even powers of S (each exchange introduces two powers of S) we need only the S^0 approximation for $\mathcal{L}^{\xi}$.

i_{ξ} , for φ_{ξ} , an argon wave function, is given by

$$i_{\xi} = (\xi | \chi \omega^{\xi} (\underline{L} \cdot \underline{\sigma})^2 | \xi) - \quad (7-22a)$$

$$- \sum_{\eta} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | \chi \underline{L} \cdot \underline{\sigma} | \xi),$$

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

This may be simplified by writing the wave functions as $\varphi^\xi = R^\xi(r) Y^\xi(\theta, \varphi) \delta(\xi)$ where $R^\xi(r)$ is the radial part of φ^ξ , $Y^\xi(\theta, \varphi)$ is its angular dependence and $\delta(\xi)$ is its spin function. Then using the unitarity of the spherical harmonics, the sum over closed shells in the second term may be simplified. The result is

$$i_\xi = \left\{ (R^\xi | \chi | R^\xi) - \sum_{\substack{\eta \\ \text{with } L \neq 0}} (R^\xi | \omega^\eta | R^\eta) (R^\eta | \chi | R^\xi) \right\} \cdot (Y^\xi \delta(\xi) | (\underline{L} \cdot \underline{\sigma})^2 | Y^\xi \delta(\xi)). \quad (7-22b)$$

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

In Section 2 of Appendix C it is shown that 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 is

$$j_{\xi\xi} = \left\{ \frac{1}{2} (R^\xi | (\frac{\partial \omega^\xi}{\partial r} + \frac{\omega^\xi}{r})^2 | R^\xi) - \right. \quad (7-23)$$

$$- \sum_{\substack{\eta \neq \xi \\ L \neq 0}} (R^\xi |\omega^\xi(r)| R^\eta)^2 (\epsilon_\eta - \epsilon_\xi) \cdot \\ \cdot (Y^\xi \delta(\xi) | (L \cdot \sigma)^2 | Y^\xi \delta(\xi)) .$$

Here we have made use of the assumption that ω^ξ is an s-like function. Under this condition we have

$$\nabla (\omega^\xi \underline{L} \cdot \underline{\sigma}) = \left[\frac{\partial \omega^\xi}{\partial r} + \frac{\omega^\xi}{r} \right] \underline{L} \cdot \underline{\sigma} \hat{r}. \quad (7-24)$$

This is the source of the first term in the equation for $j_{\xi\xi}$.

The cross term $\sum_{\eta} \frac{1}{2} (j_{\xi\eta} + j_{\eta\xi}) \mathcal{L}^\eta / j_{\xi\xi}$ is estimated in Section 2 of Appendix C. On the basis of a trial calculation in Appendix C this term is found to be less than a thousandth of the leading term for $\mathcal{L}^\xi$ and we shall neglect it. The main reason for this is the small size of the function χ where the wave function is appreciable. In atomic units, $\chi \sim 2.4 \times 10^{-4} r^{-3}$.

The cross term $K_{\eta\xi} \mathcal{L}^\eta / j_{\xi\xi}$ is of order S^2 for molecular crystals because of the $\mathcal{L}^\eta$ term and since we consider only cross terms of order S^0 , we shall ignore it.

The final cross term, $\sum_{\eta < \rho} \sum_{\xi} M_{\xi, \eta\rho} (\lambda^\eta \rho + \lambda^\rho \eta) / j_{\xi\xi}$ is similar to $\sum_{\eta < \rho} L_{\xi, \eta\rho} (\lambda^\eta \rho + \lambda^\rho \eta) / j_{\xi\xi}$ and is given by

$$\begin{aligned}
& \sum_{\eta < \rho} \sum M_{\xi, \eta \rho} (\lambda^{\eta \rho} + \lambda^{\rho \eta}) \quad (7-25) \\
& = (\lambda^{\xi^0} + \lambda^{\xi^0}) \left\{ (0_i \xi_j | u_{ij}^{\xi^0} v_{ij}^{\xi^0} \omega^{\xi^0} | \xi_j \omega^{\xi^0} | 0_i \xi_j) \right. \\
& \quad \left. - (0_i \xi_j | u_{ij}^{\xi^0} v_{ij}^{\xi^0} | 0_i \xi_j) (\xi_j | \omega^{\xi^0} | \xi_j) \right\} \\
& \quad - \sum_{\rho < \rho} (\lambda^{\rho^0} + \lambda^{\rho^0}) (0_i \rho_j | u_{ij}^{\rho^0} v_{ij}^{\rho^0} | 0_i \rho_j) (\xi_j | \omega^{\xi^0} | \xi_j)
\end{aligned}$$

Here $\eta = 0$ = the hydrogen 1s function. In deriving this we have explicitly used the assumption that only the Van der Waals interaction between the hydrogen impurity and the neighboring argon atoms will be considered. This term arises in the same way as $L_{\xi, \eta \rho}$, namely from the interaction of the Van der Waals correction factor $u_{ij}^{\xi^0}$ with the ω^{ξ^0} correction and the excess Van der Waals energy introduced by renormalization associated with the spin-orbit effect.

4. The 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 $(\lambda^{\xi \eta} + \lambda^{\eta \xi})$. Physically this simply says that we must consider the system of two atoms undergoing the Van der Waals inter-

action and not each atom separately. It amounts to using $\sum_{\xi} \sum_{\eta} (\psi^{\xi\eta}(\underline{r}_{\xi}, \underline{r}_{\eta}) + \psi^{\eta\xi}(\underline{r}_{\eta}, \underline{r}_{\xi})) \Phi_0$ as the trial wave function (rather than $\sum_{\xi} \sum_{\eta} \psi^{\xi\eta}(\underline{r}_{\xi}, \underline{r}_{\eta}) \Phi_0$ and then solving for $\psi^{\xi\eta} + \psi^{\eta\xi}$ (rather than for each $\psi^{\xi\eta}$ separately).

The Van der Waals parameter for minimum energy is given by

$$\lambda^{\xi\eta} + \lambda^{\eta\xi} = - \frac{\pi_{\xi\eta}}{Y_{\xi\eta, \xi\eta}} - \frac{\sum_{\rho} \sum_{\nu} \frac{1}{2} (Y_{\xi\nu\rho\nu} + Y_{\rho\nu, \xi\eta}) (\lambda^{\rho\nu} + \lambda^{\nu\rho}) + \sum_{\rho} L_{\rho, \xi\eta} \Lambda^{\rho} + M_{\rho, \xi\eta} \mathcal{L}^{\rho}}{Y_{\xi\eta, \xi\eta}}. \quad (7-26)$$

($\lambda^{\xi\eta} + \lambda^{\eta\xi}$) 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 we shall present here just the direct terms and leave exchange corrections to Section 3 of Appendix C.

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

$$\pi_{\xi\eta} = e^2 (\xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi_i \eta_j). \quad (7-27)$$

This term represents the electrostatic interaction between the electrons in states φ^{ξ} and φ^{η} as modified by $u_{ij}^{\xi\eta}$. It can be put in a more familiar form by adding the quantity $(\xi_i \eta_j | u_{ij}^{\xi\eta} (\frac{1}{|R_i - R_j|} - \frac{1}{|R_i - R_I|} - \frac{1}{|R_j - R_I|}) | \xi_i \eta_j)$ 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

$$\begin{aligned} \Upsilon_{\xi\eta, \xi\eta} &= \\ &= \frac{1}{2} \left\{ (\xi_i \eta_j | \nabla_i u_{ij}^{\xi\eta} \cdot \nabla_i u_{ij}^{\xi\eta} + \right. \\ &\quad \left. + \nabla_j u_{ij}^{\xi\eta} \cdot \nabla_j u_{ij}^{\xi\eta} | \xi_i \eta_j) \right\}. \end{aligned} \tag{7-28}$$

This has been obtained from the ∇^2 term by an integration by parts in the same way as $J_{\xi\xi}$ and $j_{\xi\xi}$ were calculated.

In correcting $(\lambda^{\xi\eta} + \lambda^{\eta\xi})$ for the "second generation" effects of the other variational parameters via the cross terms, we again consider only the leading terms in S^0 . Thus, no cross terms involving $\Upsilon_{\xi\eta, \rho\sigma}$

appear since these are 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 negligible compared to the leading Van der Waals terms. This can easily be seen since both Eqs. (7-27) for $\Pi_{\xi\eta}$ and (7-28) 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 contains the spin-orbit parameter $\chi = \left(\frac{\hbar^2}{4m^2c^2}\right) \frac{1}{r} \frac{\partial V}{\partial r}$ and we have shown that this leads to matrix elements of order 10^{-3} or so.

CHAPTER VIII

CALCULATION OF ELECTRON SPIN RESONANCE PARAMETERS

1. The Hyperfine and Magnetic Field Perturbations

The magnetic energy levels for a $^2S_{1/2}$ state are given by the Breit-Rabi⁵⁷ formula. This 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. By fitting electron spin resonance data for a " $^2S_{1/2}$ " center in a solid to this formula, a phenomenological description of the center may be obtained.

On the other hand, these parameters may be calculated directly from the wave function for the solid. The hyperfine interaction is given by the last term in the Hamiltonian, Eq. (5-1):

$$\begin{aligned}
 h_{h.f.s.} = & \\
 = 2\gamma\beta_e\beta_n \sum_k \left\{ \frac{(\underline{r}_k - \frac{3}{4}\underline{\sigma}_k) \cdot \underline{I}}{|\underline{r}'_k|^3} + \frac{3}{4}g \frac{(\underline{r}'_k \cdot \underline{\sigma})(\underline{r}'_k \cdot \underline{I})}{|\underline{r}'_k|^5} \right. \\
 & \left. + \frac{4\pi g}{3} \delta(\underline{r}') \underline{\sigma} \cdot \underline{I} \right\},
 \end{aligned}
 \tag{8-1}$$

where $\underline{I}$ is the spin of the hydrogen's proton and $\underline{r}'_k$ is $(\underline{r}_k - \underline{R}_H)$. This consists of two parts, the magnetic

interaction of the spin and angular momentum with the nuclear spin, and the Fermi contact interaction arising from the spin current $\underline{j}_s = -\frac{1}{2} |g| \beta \text{curl } |\phi|^2 \underline{\sigma}$ and the nuclear dipole. The latter is proportional to the density of the wave function at the nucleus, and so is non-zero only for s states.

The g factor is a measure of the interaction of the spin of the electron with the magnetic field and in general is the dyadic in the spin- $\underline{H}$ field part of the spin Hamiltonian

$$h_{\text{spin}} = \frac{\beta}{2} \underline{H} \cdot \underline{\vec{g}} \cdot \underline{\sigma}. \quad (8-2)$$

Since the experiments on hydrogen trapped in argon were done with polycrystalline samples, we shall only be concerned with the isotropic part. Thus we shall seek the coefficient of $\frac{\beta}{2} \underline{H} \cdot \underline{\sigma}$ in the interaction of the solid with the magnetic field. This will arise from the next to the last term in the Hamiltonian

$$h_{\underline{H}} = \sum_i \beta \left(\underline{L}_i + \frac{g}{2} \underline{\sigma}_i \right) \cdot \underline{H}. \quad (8-3)$$

where g is the Landé g factor for the free electron 2.00229.

Operators (8-1) and (8-3) are both sums of one-electron operators. The expectation value of these interactions for the crystal wave function (Eq. (6-6)) may be written down immediately in analogy to Eq. (7-4).

The result will be a polynomial in the variation parameters and is given in Appendix D.

We wish to calculate the spin resonance parameters to order S^2 hence, we must keep terms in Λ , $\mathcal{L}$ and λ to order S^2 . However, terms in Λ^2 , $\mathcal{L}^2$ and λ^2 and cross terms such as $\Lambda\mathcal{L}$, $\Lambda\lambda$ etc. are in a sense of second order of smallness relative to the terms of first power in the variation. On this basis, we shall consider only the S^0 contribution from these second-power terms. In this discussion we shall give the results and comments on the calculations, leaving the detailed analysis for Appendix D.

2. The g Shift

The g shift arises solely from the spin-orbit interaction correction to the argon wave functions and the fact that in the solid the wave functions of the impurity overlap the argon functions.

For the constant term ϵ' and the terms in Λ , λ , λ^2 and $\Lambda\lambda$ in the polynomial for $\langle \Phi | \hat{h}_H | \Phi \rangle$ we need only consider the $\underline{H} \cdot \underline{\sigma}$ term in Eq. (8-3) for h_H . This follows because we seek that part of the expectation value of the magnetic field interaction that is linear in $\underline{H}$ and $\underline{\sigma}$, and the operators v^z and u_{ij}^{zz} do not

contain the spin operator.

The first-order term, ϵ' , is

$$\epsilon' = \sum_{\nu} \langle \nu | \beta \frac{g}{2} \underline{H} \cdot \underline{\sigma} | \nu \rangle, \quad (8-4)$$

which sums to zero for the closed shells of the argon atoms leaving

$$\epsilon' = \frac{g}{2} \beta \underline{H} \cdot (0 | \underline{\sigma} | 0), \quad (8-5)$$

which is the interaction of one free spin, in this case the hydrogen's, with the magnetic field. Here we have used the notation $\xi = 0$ for the hydrogen 1s state.

The Λ , λ , λ^2 and $\Lambda \lambda$ contributions consist of terms of the form $\langle \nu | Q \hat{h}_H | \nu \rangle - \langle \nu | Q | \nu \rangle \langle \nu | \hat{h}_H | \nu \rangle$ or sums of terms multiplied by $\langle \nu | \hat{h}_H | \eta \rangle$, $\eta \neq \nu$ where Q is an arbitrary operator. Since Löwdin functions are spin eigenfunctions, these terms either cancel identically or are zero by orthogonality.

The g shift arises from the linear term in $\mathcal{L}^3$ which is

$$\begin{aligned} M' - \epsilon' A' = \sum_{\xi} \mathcal{L}^3 \{ & \langle \xi | \omega^3 \underline{L} \cdot \underline{\sigma} \hat{h}_H + \hat{h}_H \omega^3 \underline{L} \cdot \underline{\sigma} | \xi \rangle \\ & - \sum_{\eta} \langle \xi | \omega^3 \underline{L} \cdot \underline{\sigma} | \eta \rangle \langle \eta | \hat{h}_H | \xi \rangle \\ & - \sum_{\eta} \langle \xi | \hat{h}_H | \eta \rangle \langle \eta | \omega^3 \underline{L} \cdot \underline{\sigma} | \xi \rangle \} . \end{aligned} \quad (8-6)$$

Since the operator $\omega^3 \underline{L} \cdot \underline{\sigma}$ contains the spin operator, both the $\underline{L}$ and $\underline{\sigma}$ parts of the magnetic field interaction must be considered. Expanding the operator in the first term we have

$$\begin{aligned} \omega^3 \underline{L} \cdot \underline{\sigma} \hbar_{\underline{H}} + \hbar_{\underline{H}} \omega^3 \underline{L} \cdot \underline{\sigma} &= \\ &= \beta \omega^3 [\underline{\sigma} \cdot \vec{\Gamma} \cdot \underline{H} + g \underline{L} \cdot \underline{H}]. \quad (8-7) \end{aligned}$$

Here $\vec{\Gamma} = i [\underline{L}_i \underline{L}_j + \underline{L}_j \underline{L}_i] \hat{j}$; $i, j = \hat{x}, \hat{y}, \hat{z}$ is the operator corresponding to the g-shift tensor.

When the $\mathcal{L}$ term is expanded to order S^2 , it is found that in Eq. (8-6) the second two terms are canceled in order S^0 by the first term. Here the sum over η runs over a set that is complete for the angular operators, hence the cancellation in zeroth order. However, an S^2 term remains. The result of simplifying this S^2 term is

$$M' - \epsilon' A = -\beta \sum_{\alpha} \sum_{\beta} \mathcal{L}^{\alpha} S_{\alpha 0} S_{\beta 0} (\alpha | \omega^{\alpha} \underline{\sigma} \cdot \vec{\Gamma} \cdot \underline{H} | \beta) \quad (8-8)$$

or

$$\vec{\Delta} g = -2 \sum_{\alpha} \sum_{\beta} \mathcal{L}^{\alpha} S_{\alpha 0} S_{\beta 0} (\alpha | \omega^{\alpha} \vec{\Gamma} | \beta).$$

Here α and β are on the same atom and are either argon 2p or 3p states.

To the approximation in which we are working, we consider only S^0 terms in evaluating the contributions

to the spin resonance parameters that are proportional to $\mathcal{L}^2$, $\mathcal{L} \wedge$ and $\mathcal{L} \lambda$, since we consider these to be of second order of smallness to start with. All these terms may be treated in a manner similar to the $\mathcal{L}$ term, but as in it, the S^0 terms all cancel identically.

3. The Hyperfine Splitting

The 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 argon spin-orbit interaction makes no contribution to the splitting.

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

$$\begin{aligned} \epsilon'_{hfs} &= \frac{1}{2} \Delta A_{\text{overlap}} \frac{1}{\hbar} (0|\underline{\sigma}|0) \\ &= \frac{4\pi}{3} g \gamma \beta_e \beta_n \frac{1}{\hbar} (0|\underline{\sigma}|0) \left[\left(1 + \sum_{\alpha} S_{\alpha\alpha}^2\right) (0|\delta(\underline{r}-\underline{R}_H)|0) \right. \\ &\quad \left. - 2 \sum_{\mu} S_{\mu 0} (0|\delta(\underline{r}-\underline{R}_H)|\mu) \right]. \end{aligned} \quad (8-9)$$

Here we have used the notation $\nu = 0$ to indicate the hydrogen 1s function.

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

$$\begin{aligned}
\mu' - \epsilon' \alpha &= \frac{1}{2} \Delta A_{\text{crystal field}} \underline{I} \cdot (0 | \underline{\sigma} | 0) \\
&= -\frac{8\pi}{3} g \gamma \beta_e \beta_n \underline{I} \cdot (0 | \underline{\sigma} | 0) \Lambda^0 (0 | \underline{v}^0 | 0) (0 | \delta(\underline{r} - \underline{R}_H) | 0). \quad (8-10)
\end{aligned}$$

The Van der Waals correction makes two contributions. One which is proportional to λ appears in order S^2 ; the $S^0 \lambda$ contribution integrates to zero because of the oddness of $u^{3\gamma}$. The λ contribution is

$$\begin{aligned}
\mu' - \epsilon' \alpha &= \frac{1}{2} \Delta A_{\text{vdW}(\lambda)} \underline{I} \cdot (0 | \underline{\sigma} | 0) \quad (8-11) \\
&= \frac{8\pi}{3} g \gamma \beta_e \beta_n \underline{I} \cdot (0 | \underline{\sigma} | 0) \left\{ \sum_{\alpha \neq \gamma} (\lambda^{\alpha\gamma} + \lambda^{\gamma\alpha}) \cdot \right. \\
&\quad \left[-(a_{ij} | u_{ij}^{\alpha\gamma} \delta(\underline{r}_j - \underline{R}_H) | \gamma\alpha) + \right. \\
&\quad \left. \left. + (0 | \delta(\underline{r} - \underline{R}_H) | 0) (a_{ij} | u_{ij}^{\alpha\gamma} | \gamma\alpha) - \sum_{\alpha \neq \gamma}^{\epsilon\gamma} S_{\alpha 0} (a_{ij} | u_{ij}^{\alpha\gamma} | \gamma\alpha) \right] \right\}
\end{aligned}$$

where the symbol $\sum_{\alpha \neq \gamma}^{\epsilon\gamma}$ indicates the sum over α where φ^α and φ^γ are on the same atom, but are not equal.

The λ^2 term is the normalization correction and is

$$\begin{aligned}
n' - \epsilon' b - a[m' - \epsilon' a] &= \frac{1}{2} \Delta A_{vdw}(\lambda^2) \underline{I} \cdot (0 | \underline{\sigma} | 0) \\
&= -\frac{4\pi g}{3} \delta\beta_e \beta_\eta \underline{I} \cdot (0 | \underline{\sigma} | 0) \sum_{o < \eta} (\lambda^{o\eta} + \lambda^{\eta o}) \cdot \quad (8-12) \\
&\quad \cdot (o\eta | u_{ij}^{o\eta} | o\eta) (0 | \delta(\underline{x} - \underline{R}_H) | 0).
\end{aligned}$$

The $\Lambda \mathcal{L}$, $\mathcal{L} \lambda$ and $\Lambda \lambda$ cross terms do not contribute, the λ terms being zero to order S^0 because of the oddness of u_{ij}^{xi} and the $\mathcal{L}$ terms vanishing because of the sum over the closed shells of argon. The unpaired hydrogen spin makes no contribution to the $\mathcal{L}$ terms because the operator associated with $\mathcal{L}$ is $\omega^3 \underline{L} \cdot \underline{\sigma}$ and the hydrogen is in an $L = 0$ state.

CHAPTER IX

ORDER OF MAGNITUDE CALCULATIONS

As a sample of the calculations involved, the leading terms in the solutions for the variational parameters were evaluated and from these the hyperfine splitting and the g-shift were predicted for a hydrogen atom trapped in an octahedral site of an argon lattice. These calculations are order-of-magnitude estimates to show what terms must be studied in detail. Except for the g-shift calculation, overlap and exchange are generally ignored and the results should not be seriously compared with experiment.

1. The Overlap Integrals

Overlap integrals for the hydrogen-argon system were calculated for the outer shells of argon, and the ground and first excited states of hydrogen. The results are summarized in Fig. 2.

The hydrogen 1s-argon 3s and the hydrogen 1s-argon 3p overlaps are very nearly exponential functions over the range from 4 to 10 Bohr units. At large internuclear separations there is considerable difference between the magnitudes of the ground and excited-state overlaps. However, at smaller separations the magni-

Figure 2. Hydrogen-argon overlap integrals.

tudes are the same.

2. The Crystal Field Parameter

Neglecting terms with coefficients of S and exchange corrections, the formulas for I_0 and J_0 , where $\xi = 0$ denotes the hydrogen $1s$ state, reduce to

$$I_0 = (0|v^0 \Sigma' V_0|0) - \sum_{\eta} (0|v^0|\eta)(\eta|\Sigma' V_0|0). \quad (9-1a)$$

$$J_0 = \frac{1}{2} (0|\nabla v^0 \cdot \nabla v^0|0). \quad (9-1b)$$

In addition to the $\nabla v \cdot \nabla v$ term for J_0 , the terms

$$\begin{aligned} J_0' &= (0|v^{02} \Sigma' V_0|0) - (0|v^{02}|0)(0|\Sigma' V_0|0) \\ &\quad - 4(0|v^0|0) I_0 \end{aligned} \quad (9-1c)$$

which were neglected in deriving J_0 , were studied for comparison with the " ∇ " term.

In accord with our assumed form for $v^{\xi}(r_i)$ we choose $v^0 = |\underline{r}|^n$ where $\underline{r}$ is measured from the hydrogen nucleus. Then from the energy change $\Delta E_{\wedge \xi} = -I_{\xi}^2/J_{\xi \xi}$ for various n 's we choose the n giving the minimum total energy for use in the function. This is a minimization in two dimensions--first along $\wedge^{\xi}$ and then along η , and gives us the best wave function of the form

$$\varphi^{\circ} (1 + \Lambda^{\circ} r^n).$$

The results of evaluating the functions I_0 , J_0 , J'_0 and E_0 and Λ° are given in Table V. For $\Sigma' V_0$ the Hartree-Fock self-consistent potential for a single argon atom at $R = 6.5 a_0$ has been used.

The value of $\Delta E_{\Lambda^{\circ}}$ has been plotted against n in Fig. 3 and shows that the minimum energy occurs near $n 4.5$ at an energy of approximately -1.1×10^{-4} . From Table V it is clear that the term J'_0 plays a relatively minor role in the denominator and that the major contribution arises from the kinetic energy term of J_0 .

It is tempting to speculate what the similar minimum energy would be for the interaction between two argon atoms. In this case, there would be four outer-shell electrons giving matrix elements, namely, two 3s functions and two 3p functions. Assuming the minimum energies for each of these is approximately the same as for the hydrogen 1s function, the decrease in energy for a single atom in the argon-argon system would be approximately 4×10^{-4} ev. This is of the same order of magnitude as the observed difference at $6.5 a_0$ between the interaction of two argon atoms and the theoretical estimates made by Margenau and Kunimune. A further investigation of this effect might resolve the differ-

TABLE V

The "Crystal Field" Energy for a Hydrogen Atom in the Neighborhood of an Argon Atom

n	I_o (au)	J_o (au)	J'_o (au)	$\Lambda^o = -I_o / (J_o + J'_o)$	$E_o = -\frac{I_o^2}{J_o + J'_o}$
					ev $\times 10^{-4}$
0	0	-	-	0	0
1	-4.28×10^{-4}	0.5	-0.0003	8.56×10^{-4}	-0.10
2	-2.82×10^{-3}	6.0	-0.06	4.75×10^{-4}	-0.364
3	-1.64×10^{-2}	1.01×10^2	-2.81	1.68×10^{-4}	-0.735
4	-9.47×10^{-2}	2.52×10^3	-1.06×10^2	3.94×10^{-5}	-1.02
5	-0.555	8.90×10^4	-4.86×10^3	6.60×10^{-6}	-1.02
6	-3.31	4.21×10^6	-1.57×10^5	8.18×10^{-7}	-0.737
7	-20.0	2.60×10^8	-5.1×10^6	7.84×10^{-8}	-0.426
8	-114	1.96×10^{10}	-1.65×10^8	5.88×10^{-9}	-0.182

Figure 3.

The crystal field energy vs. n . Calculated for a hydrogen atom in the self-consistent field of an argon atom at an internuclear distance of $6.5 a_0$.

ences between the theoretical and experimental inter-atomic potentials for the rare gases⁵³ and perhaps account for the crystal structure of rare gas solids.⁵⁸

3. The Spin-Orbit Parameter

The major contribution to the g-shift will come from the argon 3p state since this is the most important non-s state overlapping the hydrogen impurity. To determine the parameter $\mathcal{L}^3$ where ξ is the argon 3p function, we shall ignore the 2p states and use $\omega^{\xi} = \frac{1}{r} n'$ where r is measured from the nucleus of the argon atom. Under these conditions Eqs. (7-22b) and (7-23) become

$$L_{\xi} = \frac{\hbar^2}{4m^2c^2} \left\{ (R^{\xi} | r^{n'-1} \frac{\partial V}{\partial r} | R^{\xi}) - \sum_{\eta} [(R^{\xi} | r^{n'} | R^{\eta}) \cdot (R^{\eta} | \frac{1}{r} \frac{\partial V}{\partial r} | R^{\xi})] \right\} \cdot (\xi | (\underline{L} \cdot \underline{\omega})^2 | \xi). \quad (9-2a)$$

$$J_{\xi\xi} = \frac{1}{2} \left\{ (R^{\xi} | (n'+1)^2 r^{2n'-2} | R^{\xi}) \right\} \cdot (\xi | (\underline{L} \cdot \underline{\omega})^2 | \xi). \quad (9-2b)$$

In evaluating these the argon self-consistent Hartree-Fock potential was fitted by an exponential.

Figure 4 summarizes the calculations. The minimum in the spin-orbit energy occurs at $n' \sim 0.9$ and the minimum energy is 5.2×10^{-3} ev. The corresponding

Figure 4.

The spin-orbit energy for the argon 3p state vs. n' .

parameter is $\mathcal{L}^{\text{Argon } 3p} \sim 57 \left(\frac{\hbar^2}{2 m c^2} \right)$.

4. The Van der Waals Parameter

To estimate the Van der Waals effect the simple dipole approximation to the interaction of two neutral charge clouds was used. Furthermore, only leading terms of order S^0 were retained and intra-atomic exchange was ignored. In this approximation Eqs. (7-22) and (7-23) become

$$\begin{aligned} \Pi_{\xi\eta} &= (\xi\eta | \frac{u_{\xi\eta}}{r_{ik}} | \xi\eta) \\ &\approx \frac{2}{3} \frac{1}{R^6} (\xi | r^2 | \xi) (\eta | r^2 | \eta). \end{aligned} \quad (9-3a)$$

$$\begin{aligned} \chi_{\xi\eta} \xi\eta &= \frac{1}{2} (\xi\eta | (\nabla_i u_{ij}^{\xi\eta} \cdot \nabla_i u_{ij}^{\xi\eta}) \\ &\quad + (\nabla_j u_{ij}^{\xi\eta} \cdot \nabla_j u_{ij}^{\xi\eta}) | \xi\eta) \\ &\approx \frac{1}{R^6} [(\xi | r^2 | \xi) + (\eta | r^2 | \eta)]. \end{aligned} \quad (9-3b)$$

Here R is the distance between the sites on which φ^ξ and φ^η are centered. In deriving these, the dipole-dipole interaction given by Eq. (6-10) has been used for both $u_{ij}^{\xi\eta}$ and the expansion of $1/r_{ij}$.

The parameter $(\lambda^{\xi\eta} + \lambda^{\eta\xi})$ is given by

$$\begin{aligned}
 (\lambda^{\xi\eta} + \lambda^{\eta\xi}) &= - \frac{\pi_{\xi\eta}}{\Upsilon_{\xi\eta, \xi\eta}} \\
 &= - \frac{2}{3} \frac{(\xi|r^2|\xi)(\eta|r^2|\eta)}{(\xi|r^2|\xi) + (\eta|r^2|\eta)}
 \end{aligned}
 \tag{9-4}$$

which is independent of R. The energy for this value of the parameter is

$$\begin{aligned}
 E_{\text{vdW}} &= - \sum_{\xi} \sum_{\eta \neq \xi} (\lambda^{\xi\eta} + \lambda^{\eta\xi}) \frac{\pi_{\xi\eta}}{\Upsilon_{\xi\eta, \xi\eta} (\lambda^{\xi\eta} + \lambda^{\eta\xi})^2} \\
 &= - \sum_{\xi} \sum_{\eta \neq \xi} \frac{\pi_{\xi\eta}^2}{\Upsilon_{\xi\eta, \xi\eta}} \\
 &= - \frac{1}{R^6} \sum_{\xi} \sum_{\eta \neq \xi} \frac{4}{9} \frac{[(\xi|r^2|\xi)(\eta|r^2|\eta)]}{(\xi|r^2|\xi) + (\eta|r^2|\eta)}.
 \end{aligned}
 \tag{9-5}$$

This minimized energy has the behavior of $1/R^6$ which is the major term in the expansion of the Van der Waals energy at large distances.

Table VI gives $\lambda = (\lambda^{\eta^0} + \lambda^{\eta})$ and individual E_{vdW} 's for the Van der Waals interaction of a hydrogen atom in the 1s state and the various shells of an argon atom, η .

From this comparison it is clear that the most important contributions come from the outer-shell

TABLE VI. Van der Waals Interaction between Hydrogen and the Subshells of Argon.

Shell	$\lambda = (\lambda^{e\gamma} + \lambda^{\gamma e})$	E_{VdW} in ev $(a_0)^6$
1s	-0.00664	$-\frac{1}{R^6}$ 3.59×10^{-3}
2s	-0.126	$-\frac{1}{R^6}$ 1.36
3p	-0.110	$-\frac{1}{R^6}$ 1.03
3s	-0.878	$-\frac{1}{R^6}$ 1.11×10^2
3p	-1.05	$-\frac{1}{R^6}$ 1.88×10^2

electrons of the argon.

Since exchange effects have been neglected, this result should not be taken seriously except as a guide to the relative importance of the various argon shells in the Van der Waals interaction. Even at large internuclear distances, Eq. (9-5) must be corrected for intratomic exchange terms. These terms, in addition to interatomic ones, are given in Appendix C.

In the limit of large internuclear separations, the effect of these exchange corrections may be seen from the work of Buckingham⁴³ who showed that Eq. (9-5) is correct for the dipole-dipole interaction if the matrix elements of r^2 are replaced with "exchange-

corrected" matrix elements defined by

$$\begin{aligned}
 (\xi | \tilde{r}^2 | \zeta) = & (\xi | r^2 | \zeta) \\
 & - \sum_{\eta \neq \xi} \left\{ (\xi | x | \eta) (\eta | x | \zeta) + (\xi | y | \eta) (\eta | y | \zeta) \right. \\
 & \left. + (\xi | z | \eta) (\eta | z | \zeta) \right\}
 \end{aligned}
 \tag{9-5a}$$

Here the sum over η runs over all occupied states centered on the same atom as φ^ξ . The net effect of this replacement is to decrease the Van der Waals energy. This brings the theoretical estimates in line with the observed values.⁵⁹

5. The g-Shift

The second line of Eq. (8-8) gives the g-shift for a system of hydrogen in argon. It is

$$\Delta \overleftrightarrow{g} = -2 \sum_{\alpha} \sum_{\beta} \overline{L}^{\alpha} S_{\alpha 0} S_{\beta 0} (\alpha | \omega^{\alpha} \overleftrightarrow{r} | \beta)
 \tag{9-6}$$

where $\overleftrightarrow{r} = \hat{i} (L_i L_j + L_j L_i) \hat{j}$. For an example let us consider the isotropic g-shift for a hydrogen atom in an octahedral site. The geometry for this is shown in Fig. 5.

Non-zero overlap occurs only for σ states, that is for states with projected angular momentum, m_L ,

Figure 5.

The geometry of an octahedral trapping site showing a central hydrogen atom surrounded by six argon atoms.

zero along the line joining the hydrogen-argon nuclei. Hence, for the magnetic field as shown, atoms in positions A make no contribution to the diagonal term of $\hat{T}$ since both overlaps involve just σ states which have zero $(L_z)^2$. On the other hand, atoms in positions B do contribute, since the σ states are linear combinations of $L_z = +1$ and $L_z = -1$ states. The result for the isotropic g-shift is from Eq. (9-6)

$$\Delta g = -4 \sum_{\alpha} \sum_{\beta} \mathcal{L}^{\alpha} S_{\alpha\alpha} S_{\beta\beta} (\alpha | \omega^{\alpha} (L_z)^2 | \beta) \quad (9-7)$$

where non-zero contributions to the sum of $L_z^2 = 1$ will come from the four atoms at B.

Figure 6 shows Δg for an octahedral site plotted against the argon-hydrogen internuclear distance. Here we see that the g-shift is negative and increases as the internuclear distance decreases.

6. The Hyperfine Interaction

Neglecting exchange terms in the first power of $(\lambda^{\xi\eta} + \lambda^{\eta\xi})$, the changes in the hyperfine interaction are given by Eqs. (9-8a), (9-8b) and (9-8c) respectively. These are the corrections to the free atomic interaction introduced by (1) renormalization after orthogonalizing; (2) the crystal field, and (3) the Van

Figure 6.

The g-shift for a hydrogen atom trapped in an argon lattice. These results are for an octahedral trapping site with neighbors at a distance R from the trapped atom.

der Waals interaction.

$$\Delta A_{\text{overlap}} = \frac{8\pi g}{3} \gamma \beta_e \beta_n \left[\sum_{\alpha} S_{\alpha}^2 (0 | \delta(\underline{r} - \underline{R}_H) | 0) - \right. \\ \left. - 2 \sum_{\mu} S_{\mu 0} (0 | \delta(\underline{r} - \underline{R}_H) | \mu) \right] \quad (9-8a)$$

$$\Delta A_{\text{crystal field}} = -\frac{16\pi g}{3} \gamma \beta_e \beta_n (0 | \delta(\underline{r} - \underline{R}_H) | 0) \cdot \\ \Lambda^0 (0 | v^0 | 0) \quad (9-8b)$$

$$\Delta A_{\text{vdw}}(\lambda^2) = -\frac{8\pi g}{3} \gamma \beta_e \beta_n (0 | \delta(\underline{r} - \underline{R}_H) | 0) \\ \sum_{0 < \eta} (\lambda^{\eta} + \lambda^{\eta 0})^2 (0 | \eta | (u_{ij}^{\eta})^2 | 0 \eta) \quad (9-8c)$$

Table VII and Fig. 7 summarize the numerical values of these contributions to the hyperfine interaction. Although only one value of Λ^0 was calculated for $R = 6.5a_0$, Λ^0 was estimated for R greater than $6.5a_0$ by assuming an S^2 dependence on R . (For R less than $6.5a_0$, this is not a safe procedure because the overlap terms in Eq. (C-6) would tend to cancel the effect of the crystal field and Λ^0 does not increase as rapidly as S^2 .)

TABLE VII

Fractional Change in Hyperfine Interaction of a Hydrogen Atom at Distance R from
an Argon Atom

These are order-of-magnitude estimates in which exchange effects have been ignored.

R	CONTRIBUTIONS TO A/A %			TOTAL A/A %	
	<u>a</u> Orthogonalization	<u>b</u> Crystal Field	<u>c</u> Van der Waals	a + c	a + b + c
5	1.30	-	-0.648	0.65	-
6.5	0.140	-0.136	-0.134	0.006	-0.13
7.1	0.0552	-0.043 *	-0.0790	-0.024	-0.067
8	0.0126	-0.010 *	-0.0385	-0.026	-0.036
10	0.00042	-0.0001 *	-0.0100	-0.010	-0.010

* estimated

Fig. 7. The shift in hyperfine splitting for a hydrogen atom trapped in an argon lattice. These results are for an octahedral trapping site with neighbors at a distance R from the trapped atom.

CHAPTER X

CONCLUSIONS AND COMPARISON WITH PREVIOUS WORK

In this study an attempt has been made to make a calculation correct to second order in overlap for the wave function and the electron-spin-resonance parameters of a paramagnetic tight-binding center in a rare gas crystal. 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.

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 electron correlation.

In this approach, all the effects are included simultaneously so that cross terms depending on two different effects in the crystal are not omitted. In previous studies, the effect of each interaction has been calculated separately and the results added.

The results indicate that provided there is no overlap, it is a good approximation to calculate effects separately and add. This conclusion is not generally valid, however, and indeed, if there is appreciable overlap, this procedure is not justified. In the latter case the intra-atomic potentials of the atoms neighboring the impurity must be taken into account as a crystal field. Furthermore, the electron correlation or 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 of overlap of an electron centered on the impurity with neighboring atoms in which spin-orbit interactions occur. The g-shift is independent of crystal field and correlation effects and, from the results of this study, it appears to be the most reliably calculated parameter for a tight-binding center in a molecular crystal, provided the geometry of the trapping site is known.

The shift in the g-tensor for hydrogen in argon is given by Eq. (9-6),

$$\Delta \hat{g} = -2 \sum_{\alpha} \sum_{\beta} L^{\alpha} S_{\alpha 0} S_{\beta} (\alpha | w^{\alpha} \hat{r} | \beta), \quad (9-6)$$

where $\sum = 0$ represents the hydrogen 1s state and

the sums over α and β run over the argon states. The operator $\hat{T}$ is given by $\hat{T} = \hat{i} [L_1 L_j + L_j L_1] \hat{j}$. The g-shift is of second order in overlap and is directly proportional to the spin-orbit correction to the argon wave functions.

If only one p function of the argon atom, has appreciable overlap with the hydrogen atom, the diagonal or isotropic g-shift is given by

$$\Delta g = -4 S_{\alpha 0}^2 \mathcal{L}^{\alpha}(\varphi^{\alpha} | \omega^{\alpha} | \varphi^{\alpha})(\varphi^{\alpha} | L_z^2 | \varphi^{\alpha}) \quad (10-1)$$

where we have separated the radial and angular parts of the matrix elements.

This is to be compared with Adrian's result for the isotropic g-shift given by Eq. (E-12),

$$\Delta g = \frac{4}{3 \bar{E}_h} S_{\alpha 0}^2 \lambda_{\alpha} (\varphi^{\alpha} | L_z^2 | \varphi^{\alpha}). \quad (E-12)$$

In both cases the g-shift is proportional to S^2 and $(\varphi^{\alpha} | L_z^2 | \varphi^{\alpha})$. However, Adrian's result contains the average excitation energy for hydrogen, $\bar{E}_h$, whereas the present result contains no such quantity. Indeed, $\mathcal{L}^{\alpha}(\varphi^{\alpha} | \omega^{\alpha} | \varphi^{\alpha})$ is determined entirely by the argon center.

Physically the g-shift can be thought of as aris-

ing because the electron centered on the hydrogen site spends some of its time moving in an argon p state. In this state it experiences a spin-orbit interaction which mixes spin and orbital functions. This coupled with the splitting of the argon p states by the $\underline{H} \cdot \underline{L}$ part of the magnetic field interaction leads to an energy term equivalent to an $\underline{H} \cdot \underline{\sigma}$ term in the spin Hamiltonian.

Since this mechanism is concerned with only the argon atom, the g-shift should depend on the spin-orbit effect for the argon wave function. Moreover, it seems unreasonable that it should depend on any property of the hydrogen atom such as the average excitation energy.

The results of evaluating (9-7) assuming a contribution from the 3p shell of argon only are plotted with Adrian's results in Fig. 6. Considering the differences in the derivations, the agreement between the predicted values of the two theories is surprising since, to the accuracy of the numerical methods used, they are identical.

The essential difference between Adrian's calculation and the present theory is that Adrian applied second-order perturbation theory to the one-electron hydrogen wave function modified for exchange, and that here the entire crystal wave function is considered.

In applying the usual sum rule to the results of second-order perturbation theory in Adrian's picture one would be tempted to use the average excitation energy for the hydrogen atom. However, before applying the sum rule, the g-shift is given by

$$\begin{aligned} \Delta g = & \\ & = \frac{\hbar^2}{m^2 c^2} \sum_{\varphi} \langle \varphi^0 - S_{0, A3P\sigma} \varphi^{A3P\sigma} | \frac{1}{r} \frac{\partial V}{\partial r} L_z | \varphi \rangle \cdot \\ & \quad \langle \varphi | L_z | \varphi^0 - S_{0, A3P\sigma} \varphi^{A3P\sigma} \rangle. \end{aligned} \quad (10-1)$$

Here we have used Eqs. (E-9) and (E-10) and neglected the normalization correction.

If hydrogen functions are used for the φ 's the terms give a contribution to Δg of fourth order in overlap which is negligible. If, on the other hand, one uses argon functions, the contributions are of order S^2 . The most convenient set of excited states is therefore the argon states and the average excitation energy should be that for argon. Another statement of the same thing is to say that besides the excited hydrogen states, one must also include all the possible excited states of the crystal. If the average excitation energy of argon is calcu-

lated by Adrian's prescription*, we find a value of 13.4 ev. This is less than 13% larger than the average energy for hydrogen, viz. 11.9 ev, that Adrian used in his calculations. Another possible estimate of the argon excitation energy for the solid is the exciton absorption-band energy. From Knox and Bassani's extrapolation⁶⁰ of the work of Schnepf and Dressler⁶¹, exciton absorption will occur somewhere in the vicinity of 11.5 to 12.0 ev. From these estimates, the close agreement between the two predictions of the g-shift would seem to be accidental.

In addition to the theoretical curves, two "experimental" g-shifts are shown in Fig. 6. In plotting these the assignments to undistorted lattice sites made by Foner et al.¹¹ have been used**. The point for the substitutional site is plotted on the graph for the octahedral site as half the observed shift since there are twice as many nearest neighbors for such sites. Although the theory seems to agree reasonably with this assignment of trapping sites, the lack of knowledge

* Adrian took the average excitation energy as the average of the energy of the first excited state and of the ionization energy.

** Foner et al.¹¹ make assignments only to the substitutional and octahedral sites. They believe that "energetic considerations" prevent occupancy of the tetrahedral site in the conditions of their experiment.

about lattice relaxation makes comparison difficult. It should be pointed out, however, that the predictions for the present theory would be shifted toward greater g-shifts at small internuclear separations if the effect of argon 2p states were included. This would improve the agreement with the "experimental" points as they are plotted.

A possible experimental test of the two points of view on the g-shift is to study the alkali atoms as impurities in argon. For this series of elements with one electron outside a closed shell, the g-shift for a given site should be proportional to a constant times the square of the overlap integral if the present theory holds. For Adrian's theory it should be that divided by the average excitation energy of the impurity.

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 effect, 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.

The shift in hyperfine interaction due to orthogonalization (overlap) is given by Eq. (8-9); it is

$$\Delta A_{\text{overlap}} = \frac{8\pi g}{3} \gamma \beta_e \beta_n \left[\sum_{\alpha} S_{\alpha}^2 (0 | \delta(\underline{r} - \underline{R}_H) | 0) - \right. \\ \left. - 2 \sum_{\mu} S_{\mu 0} (0 | \delta(\underline{r} - \underline{R}_H) | \mu) \right]. \quad (8-9)$$

This is to be compared with Adrian's result, Eq. (E-8)

$$\Delta A_{\text{overlap}} = \frac{8\pi g}{3} \gamma \beta_e \beta_n \left[\sum_{\alpha} S_{\alpha}^2 (0 | \delta(\underline{r} - \underline{R}_H) | 0) \right] \quad (E-8)$$

where $\delta(\underline{r} - \underline{R}_H)$ is the Dirac δ function centered on the hydrogen nucleus.

These two equations differ by the term $(0 | \delta(\underline{r} - \underline{R}_H) | \mu)$ that occurs in the present result. The first part of (8-9) (Adrian's result) is just 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, ψ^0 , and the argon functions, ψ^{μ} , admixed by orthogonalization. Sample calculations indicate that at small internuclear distances this new term is important. For example, at $R = 5a_0$ it is 15% of the leading term whereas at $R = 10a_0$ it is only a 3% correction. Numerical estimates of the shift in hyperfine interaction due to wave function overlap are given in column a of Table VII. It always represents a positive correction.

The shift in hyperfine interaction associated with the crystal field is a normalization correction to the electron density at the nucleus of the hydrogen atom. It is given by Eq. (8-10)

$$\Delta A_{\text{crystal field}} = -\frac{16\pi g}{3} \gamma \beta_e \beta_n (0|\delta(\underline{r}-\underline{R}_H)|0) \cdot \Lambda^0 (0|\psi^0|0). \quad (8-10)$$

This term has no counterpart in Adrian's study which is essentially a "point ion" approximation. Numerical estimates of Λ^0 indicate that this effect is of order S^2 as one might expect because the crystal field is localized within the atoms.

Calculation of Λ^0 is complicated by several complex exchange terms (see Eq. (7-17) for I_{ξ}). From the work of Phillips⁶², considerable cancellation of the direct matrix elements of the atomic potentials by the exchange matrix elements is to be expected. In the order-of-magnitude calculations only the direct terms were estimated. Their contribution to the hyperfine splitting is given in column b of Table VII. These values are an upper limit to the crystal field effect and probably overestimate it by a factor of five or ten.

The Van der Waals or correlation effect produces

two shifts. One is proportional to $(\lambda^{\circ\eta} + \lambda^{\eta\circ})$ and is of order S^2 . The other is a term of order S^0 in $(\lambda^{\circ\eta} + \lambda^{\eta\circ})^2$. The first is given by Eq. (8-11) and is

$$\begin{aligned} \Delta A_{vdw}(\lambda) &= \frac{16\pi g}{3} \gamma \beta_e \beta_\eta \cdot \\ &\sum_{\eta} (\lambda^{\circ\eta} + \lambda^{\eta\circ}) \left\{ -(0_i \eta | u_{ij}^{\circ\eta} \delta(\underline{r}_j - \underline{R}_H) | \eta 0_j) \right. \\ &\quad + (0 | \delta(\underline{r} - \underline{R}_H) | 0) [(0_i \eta | u_{ij}^{\circ\eta} | \eta 0_j) - \\ &\quad \left. - \sum_{\alpha \neq \eta}^{\epsilon \eta} S_{\alpha 0} (0_i \eta | u_{ij}^{\circ\eta} | \eta \alpha_j)] \right\}. \end{aligned} \quad (8-11)$$

This does not arise in Adrian's treatment since it represents a cross term resulting from orthogonalization and the Van der Waals interaction. No estimates of this term have yet been made.

The $(\lambda^{\circ\eta} + \lambda^{\eta\circ})^2$ term arises from the renormalization of the hydrogen's wave function caused by the Van der Waals correction. It is given by Eq. (8-12)

$$\begin{aligned} \Delta A_{vdw}(\lambda^2) &= -\frac{8\pi g}{3} \gamma \beta_e \beta_\eta (0 | \delta(\underline{r} - \underline{R}_H) | 0) \quad (8-12) \\ &\sum_{\alpha < \eta} (\lambda^{\circ\eta} + \lambda^{\eta\circ})^2 (0_i \eta | (u_{ij}^{\circ\eta})^2 | 0_i \eta). \end{aligned}$$

This result is to be compared with Adrian's, which is given by Eq. (E-7),

$$\Delta A_{\text{vdw}} = - \frac{8\pi q}{3} \gamma \beta_e \beta_n \langle 0 | \delta(\underline{r} - \underline{R}_H) | 0 \rangle \quad (\text{E-7}')$$

$$\left(\frac{2}{\bar{E}_H} + \frac{1}{\bar{E}_H + \bar{E}_A} \right) E_{\text{vdw}}.$$

where $\bar{E}_H$ is the average excitation energy of hydrogen, $\bar{E}_A$ is the average excitation energy of argon and E_{vdw} is the Van der Waals energy for the interaction between a hydrogen atom and an argon atom. From the work of Bender³⁵ and Herman³⁶ the $2/E$ term represents the shift due to the difference in dipole moments for the two hyperfine states of hydrogen. We have ignored this effect in deriving (8-9) so our result should strictly be compared only with the $1/(\bar{E}_H + \bar{E}_A)$ part of Eq.(E-7).

To make the reduction of our result for the Van der Waals shift in the hyperfine interaction, Eq. (8-12), to Adrian's, we neglect overlap effects and use only the dipole-dipole terms in the expansion for $1/r_{ij}$. The result can be written as

$$\Delta A_{\text{vdw}}(\lambda^2) \approx - \frac{8\pi q}{3} \gamma \beta_e \beta_n \langle 0 | \delta(\underline{r} - \underline{R}_H) | 0 \rangle \sum_{o < \gamma} (\lambda^{o\gamma} + \lambda^{\gamma o}) (E_{\text{vdw}})_{o\gamma} \quad (8-12a)$$

Comparison of this with the $1/\bar{E}_H + \bar{E}_A$ term of Eq. (E-7) shows that $(\lambda^{\text{on}} + \lambda^{\text{no}})$ represents the reciprocal of an energy denominator. Numerical estimates of this term are given in column c of Table VII. Since overlap is neglected the results should be considered as an indication of the order of magnitude only.

The last two columns of Table VII give order-of-magnitude estimates of the net shift in hyperfine interaction. Two results are given. The first column labeled "a + c" gives the sum of the shifts due to orthogonalization and the Van der Waals interaction (columns a and c respectively). Here complete cancellation of the crystal field effects by the exchange terms in Eq. (7-17) for I_{ξ} is assumed. The second column labeled "a + b + c" gives the sum of the orthogonalization, crystal field and Van der Waals shifts (columns a, b and c). In calculating the latter results no exchange effects have been included.

Considering the success of the point ion approximation in so many problems, the cancellation of the crystal field terms probably occurs to a large extent for hydrogen in argon. Hence, the first set of results (column a + b) gives the best picture of the shifts in the hyperfine splitting.

Adrian's results for the shift in hyperfine splitting together with our order-of-magnitude estimates are given in Fig. 7. There is general similarity between Adrian's results and our estimates when the crystal field is neglected in the present theory. If the crystal field effect is included, but provision is not made for the cancellation due to exchange matrix elements, unreasonable hyperfine shifts are predicted at small internuclear distances. Agreement with the "experimental" points is reasonable for both Adrian's results and our order-of-magnitude calculations if the crystal field cancellation is assumed.

In general one can say that Adrian's treatment of the hyperfine splitting is valid provided there is no overlap and the internuclear separation is sufficient so that the electrostatic interaction is given reasonably well by the first two terms of the binomial expansion. At smaller internuclear separations great care must be exercised to include the effects of the crystal field and exchange matrix elements. The present theory provides the framework for such a calculation, but complete evaluation of the exchange terms must be made before the crystalline field is understood.

APPENDIX A

EXPANSION OF MATRIX ELEMENTS INVOLVING ANTISYMMETRIC WAVE FUNCTIONS

In order to evaluate matrix elements like $\langle u_0 | \mathcal{H}' | u_0 \rangle$, $\langle u_1 | \mathcal{H}' | u_0 \rangle$, $\langle u_1 | \mathcal{H}' | u_1 \rangle$, etc., it is necessary to expand the wave functions u_0 , u_1 , etc. into the antisymmetrized product form and find the matrix elements in terms of the one-electron functions. This task is made considerably easier if the one-electron functions are orthogonal. Since then, on integrations over a particular coordinate $\underline{r}_i$, the matrix element is zero unless: a) the wave functions of coordinate $\underline{r}_i$ in both the bra and the ket are the same or b) if different, that the operator contains a function of $\underline{r}_i$.

For a guide to the developments of the formulas in Appendix C and for easy reference we tabulate the expanded form of these matrix elements. The method of evaluation is most easily given by example. In the simplest case we have

$$\begin{aligned}
\langle u_0 | u_0 \rangle &= \langle a \Phi_0 | a \Phi_0 \rangle \\
&= \frac{1}{N!} \langle \sum_P (-1)^P P \Phi_0 | \sum_{P'} (-1)^{P'} P' \Phi_0 \rangle \quad (A-1a) \\
&= \frac{1}{N!} \sum_P (-1)^P P \langle \Phi_0 | (-1)^P \sum_{P'} (-1)^{-P+P'} P^{-1} P' | \Phi_0 \rangle \\
&= \frac{1}{N!} \sum_P (-1)^{2P} P \langle \Phi_0 | \sum_{P''} (-1)^{P''} P'' \Phi_0 \rangle
\end{aligned}$$

Here we have combined the product of P' and P^{-1} into a new permutation operator P'' . However, $\sum_P P$ operating on the matrix element (a constant under P) just gives a coefficient $N!$ which cancels the denominator. Hence,

$$\langle u_0 | u_0 \rangle = \langle \Phi_0 | \sum_{P''} (-1)^{P''} P'' \Phi_0 \rangle \quad (A-1b)$$

This result simply states that while there are $N!$ different bras and $N!$ different kets, because of the integration, one of the permutations and the $\frac{1}{N!}$ are unnecessary. In this work we will consider only permutations of the kets.

Using the orthogonality of the one-electron functions, Eq. (A-1b) gives

$$\langle u_0 | u_0 \rangle = 1 \quad (A-1c)$$

While this example is a difficult way of getting an obvious result, it shows the method. A somewhat less intuitive example is:

$$\begin{aligned}
\langle u_1 | u_1 \rangle &= \langle a \sum_{\xi} \varepsilon^{\xi}(\underline{r}_{\xi}) \Phi_0 | a \sum_{\eta} \varepsilon^{\eta}(\underline{r}_{\eta}) \Phi_0 \rangle \\
&= \langle \sum_{\xi} \varepsilon^{\xi}(\underline{r}_{\xi}) \Phi_0 | \sum_{\eta} (-1)^P P (\sum_{\eta} \varepsilon^{\eta}(\underline{r}_{\eta}) \Phi_0) \rangle \\
&= \sum_{\xi} \langle \phi^{\xi} | \varepsilon_i^{\xi^2} | \phi^{\xi} \rangle \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \phi_i^{\xi} \phi_j^{\eta} | \varepsilon_i^{\xi} \varepsilon_j^{\eta} | \phi_i^{\xi} \phi_j^{\eta} \rangle \quad (A-2) \\
&\quad - \sum_{\xi} \sum_{\eta \neq \xi} \langle \phi_i^{\xi} \phi_j^{\eta} | \varepsilon_i^{\xi} \varepsilon_j^{\xi} | \phi_i^{\eta} \phi_j^{\xi} \rangle.
\end{aligned}$$

The last line follows since, at most, there can be only two different coordinates over which the integrals are not zero by the orthogonality conditions.

Rather than write out all the exchange terms, we shall sometimes use the abbreviation $\overset{n}{\longleftrightarrow}$ where n represents the number of such terms. Thus in this notation Eq. (A-2) becomes

$$\begin{aligned}
\langle u_1 | u_1 \rangle &= \sum_{\xi} \langle \phi^{\xi} | \varepsilon^{\xi^2} | \phi^{\xi} \rangle \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \phi_i^{\xi} \phi_j^{\eta} | \varepsilon_i^{\xi} \varepsilon_j^{\eta} | \phi_i^{\xi} \phi_j^{\eta} \rangle - \overset{1}{\longleftrightarrow} \quad (A-3)
\end{aligned}$$

Here the $\overset{1}{\longleftrightarrow}$ instructs us to supply one term with ξ and η exchanged in the ket. Of course this includes changing ε_j^{η} to ε_j^{ξ} in the operator since this term originated in the ket. Care must be taken to give the correct sign, $(-1)^P$, to the exchange terms when supply-

ing them.

In treating the $\langle u_3 | u_3 \rangle$ and $\langle u_3 | u'_3 | u_3 \rangle$ terms, we shall exclude terms involving $u_{ij}^{\xi\eta} u_{ij}^{\nu\mu}$ where ν and μ are not either ξ or η . While these terms occur in the final expansion, they represent three-body interaction terms as far as this work is concerned and are of no interest.

For economy in writing we shall denote wave functions by their quantum number index. Thus $\langle \phi^\xi | \mathcal{E}^{\xi^2} | \phi^\xi \rangle$ will be written as $\langle \xi | \mathcal{E}^{\xi^2} | \xi \rangle$. To indicate with which coordinate a given one-electron function is associated, we shall subscript the quantum number index with the coordinate index. In this notation $\langle \phi^\xi(r_i) \phi^\eta(r_j) \phi^p(r_k) \rangle$ would be written $\langle \xi_i \eta_j p_k |$.

SUMMARY OF EXPANSIONS

NORMALIZATION MATRIX ELEMENTS

$$\langle u_0 | u_0 \rangle = 1$$

$$\langle u_1 | u_0 \rangle = \langle u_1 | u_0 \rangle = \sum_{\xi} \langle \xi | \mathcal{E}^{\xi} | \xi \rangle$$

$$\begin{aligned} \langle u_1 | u_1 \rangle &= \sum_{\xi} \langle \xi | \mathcal{E}^{\xi^2} | \xi \rangle \\ &+ \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_i \eta_j | \mathcal{E}^{\xi} \mathcal{E}^{\eta} | \xi_i \eta_j \rangle - \longleftrightarrow \end{aligned}$$

$$\langle u_3 | u_0 \rangle = \langle u_0 | u_3 \rangle$$

$$= \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} | \eta_i \xi_j \rangle$$

$$\begin{aligned} \langle u_3 | u_3 \rangle &= \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{Y}_{ij}^{\eta\xi} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{Y}_{ij}^{\eta\xi} | \eta_i \xi_j \rangle \\ &\quad + \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{Y}_{ij}^{\eta\xi} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{Y}_{ij}^{\eta\xi} | \eta_i \xi_j \rangle \end{aligned}$$

$$\langle u_3 | u_1 \rangle = \langle u_1 | u_3 \rangle$$

$$\begin{aligned} &= \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{E}_i^{\xi} | \xi_i \eta_j \rangle - \hookrightarrow \\ &\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{E}_j^{\eta} | \xi_i \eta_j \rangle - \hookrightarrow \\ &\quad + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \langle \xi_i \eta_j p_k | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{E}_k^p | \xi_i \eta_j p_k \rangle - \hookrightarrow \end{aligned}$$

HAMILTONIAN MATRIX ELEMENTS

$$\mathcal{H} = W + \sum_i H_i + \sum'_{ij} G_{ij}$$

$$\begin{aligned} \langle u_0 | \mathcal{H} | u_0 \rangle &= W + \sum_{\xi} \langle \xi_i | H_i | \xi_i \rangle \\ &\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_i \eta_j | G_{ij} | \xi_i \eta_j \rangle - \hookrightarrow \end{aligned}$$

$$\langle u_1 | \mathcal{H} | u_0 \rangle = \langle u_0 | \mathcal{H} | u_1 \rangle$$

$$\begin{aligned} &= W \sum_{\xi} \langle \xi_i | \mathcal{E}_i^{\xi} | \xi_i \rangle \\ &\quad + \sum_{\xi} \langle \xi_i | \mathcal{E}_i^{\xi} H_i | \xi_i \rangle \\ &\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_i \eta_j | \mathcal{E}_i^{\xi} H_j | \xi_i \eta_j \rangle - \hookrightarrow \\ &\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_i \eta_j | \mathcal{E}_i^{\xi} (G_{ij} + G_{ji}) | \xi_i \eta_j \rangle - \hookrightarrow \\ &\quad + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \langle \xi_i \eta_j p_k | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{E}_k^p | \xi_i \eta_j p_k \rangle \\ &\quad - \hookrightarrow \end{aligned}$$

$$\begin{aligned}
\langle u_1 | \mathcal{H} | u_1 \rangle &= W \left[\sum_{\xi} \langle \xi | \mathcal{E}^{\xi^2} | \xi \rangle \right. \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi; \eta_j | \mathcal{E}_i^{\xi} \mathcal{E}_j^{\eta} | \xi; \eta_j \rangle - \leftarrow^1 \\
&\quad + \sum_{\xi} \langle \xi_i | \mathcal{E}_i^{\xi} H_i \mathcal{E}_i^{\xi} | \xi_i \rangle \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi; \eta_j | \mathcal{E}_i^{\xi^2} H_j | \xi; \eta_j \rangle - \leftarrow^1 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi; \eta_j | \mathcal{E}_i^{\xi} (H_i + H_j) \mathcal{E}_j^{\eta} | \xi; \eta_j \rangle - \leftarrow^1 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \langle \xi; \eta_j p_k | \mathcal{E}_i^{\xi} H_k \mathcal{E}_j^{\eta} | \xi; \eta_j p_k \rangle - \leftarrow^5 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi; \eta_j | \mathcal{E}_i^{\xi} (G_{ij} + G_{ji}) \mathcal{E}_i^{\xi} | \xi; \eta_j \rangle - \leftarrow^1 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \langle \xi; \eta_j p_k | \mathcal{E}_i^{\xi^2} G_{jk} | \xi; \eta_j p_k \rangle - \leftarrow^5 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi; \eta_j | \mathcal{E}_i^{\xi} (G_{ij} + G_{ji}) \mathcal{E}_j^{\eta} | \xi; \eta_j \rangle - \leftarrow^1 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \left[\langle \xi; \eta_j p_k | \mathcal{E}_i^{\xi} (G_{ik} + G_{ki}) \mathcal{E}_j^{\eta} | \xi; \eta_j p_k \rangle \right. \\
&\quad \quad \left. + \langle \xi; \eta_j p_k | \mathcal{E}_i^{\xi} (G_{jk} + G_{kj}) \mathcal{E}_j^{\eta} | \xi; \eta_j p_k \rangle \right] - \leftarrow^5 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \sum_{v \neq \xi} \langle \xi; \eta_j p_k v_l | \mathcal{E}_i^{\xi} G_{kl} \mathcal{E}_j^{\eta} | \xi; \eta_j p_k v_l \rangle - \leftarrow^{23}
\end{aligned}$$

$$\begin{aligned}
\langle u_3 | \mathcal{H} | u_0 \rangle &= \langle u_0 | \mathcal{H} | u_3 \rangle \\
&= W \left[\sum_{\xi} \sum_{\eta \neq \xi} \langle \xi; \eta_j | \mathcal{Y}_{ij}^{\xi \eta} | \xi; \eta_j \rangle - \leftarrow^1 \right] \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi; \eta_j | \mathcal{Y}_{ij}^{\xi \eta} (H_i + H_j) | \xi; \eta_j \rangle - \leftarrow^1 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \langle \xi; \eta_j p_k | \mathcal{Y}_{ij}^{\xi \eta} H_k | \xi; \eta_j p_k \rangle - \leftarrow^1 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi; \eta_j | \mathcal{Y}_{ij}^{\xi \eta} (G_{ij} + G_{ji}) | \xi; \eta_j \rangle - \leftarrow^1 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \langle \xi; \eta_j p_k | \mathcal{Y}_{ij}^{\xi \eta} (G_{ik} + G_{ki} + \\
&\quad \quad + G_{jk} + G_{kj}) | \xi; \eta_j p_k \rangle - \leftarrow^5 \\
&\quad + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \sum_{v \neq \xi} \langle \xi; \eta_j p_k v_l | \mathcal{Y}_{ij}^{\xi \eta} G_{kl} | \xi; \eta_j p_k v_l \rangle - \leftarrow^{23}
\end{aligned}$$

$$\langle u_3 | \mathcal{H} | u_3 \rangle =$$

$$\begin{aligned}
&= W [\langle \xi_i \eta_j | \mathcal{H}_{ij}^{\xi\eta} \mathcal{H}_{ij}^{\xi\eta} | \xi_i \eta_j \rangle - \langle 1 \rangle \\
&\quad + \langle \xi_i \eta_j | \mathcal{H}_{ij}^{\xi\eta} \mathcal{H}_{ij}^{\eta\xi} | \xi_i \eta_j \rangle - \langle 1 \rangle] \\
&\quad + \langle \xi_i \eta_j | \mathcal{H}_{ij}^{\xi\eta} (H_i + H_j) \mathcal{H}_{ij}^{\xi\eta} | \xi_i \eta_j \rangle - \langle 1 \rangle \\
&\quad + \langle \xi_i \eta_j p_k | \mathcal{H}_{ij}^{\xi\eta} H_k \mathcal{H}_{ij}^{\xi\eta} | \xi_i \eta_j p_k \rangle - \langle 5 \rangle \\
&\quad + \langle \xi_i \eta_j | \mathcal{H}_{ij}^{\xi\eta} (H_i + H_j) \mathcal{H}_{ij}^{\eta\xi} | \xi_i \eta_j \rangle - \langle 1 \rangle \\
&\quad + \langle \xi_i \eta_j p_k | \mathcal{H}_{ij}^{\xi\eta} H_k \mathcal{H}_{ij}^{\eta\xi} | \xi_i \eta_j p_k \rangle - \langle 5 \rangle \\
&\quad + \langle \xi_i \eta_j | \mathcal{H}_{ij}^{\xi\eta} (G_{ij} + G_{ji}) \mathcal{H}_{ij}^{\xi\eta} | \xi_i \eta_j \rangle - \langle 1 \rangle \\
&\quad + \langle \xi_i \eta_j p_k | \mathcal{H}_{ij}^{\xi\eta} (G_{ik} + G_{ki} + \\
&\quad \quad G_{jk} + G_{kj}) \mathcal{H}_{ij}^{\xi\eta} | \xi_i \eta_j p_k \rangle - \langle 5 \rangle \\
&\quad + \langle \xi_i \eta_j p_k \sigma_l | \mathcal{H}_{ij}^{\xi\eta} G_{kl} \mathcal{H}_{ij}^{\xi\eta} | \xi_i \eta_j p_k \sigma_l \rangle - \langle 23 \rangle \\
&\quad + \langle \xi_i \eta_j | \mathcal{H}_{ij}^{\xi\eta} (G_{ij} + G_{ji}) \mathcal{H}_{ij}^{\eta\xi} | \xi_i \eta_j \rangle - \langle 1 \rangle \\
&\quad + \langle \xi_i \eta_j p_k | \mathcal{H}_{ij}^{\xi\eta} (G_{ik} + G_{ki} + \\
&\quad \quad + G_{jk} + G_{kj}) \mathcal{H}_{ij}^{\eta\xi} | \xi_i \eta_j p_k \rangle - \langle 5 \rangle \\
&\quad + \langle \xi_i \eta_j p_k \sigma_l | \mathcal{H}_{ij}^{\xi\eta} G_{kl} \mathcal{H}_{ij}^{\eta\xi} | \xi_i \eta_j p_k \sigma_l \rangle - \\
&\quad \quad - \langle 23 \rangle
\end{aligned}$$

Note: Here and on the next page the summation signs have been dropped to simplify the formulas.

$$\langle u_3 | \mathcal{H} | u_1 \rangle =$$

$$\begin{aligned}
&= V \left[\langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{E}_i^{\xi} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{E}_i^{\eta} | \eta_i \xi_j \rangle \right. \\
&\quad \left. \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{E}_j^{\eta} | \xi_i \eta_j \rangle - \overset{1}{\leftarrow} \right. \\
&\quad \left. \langle \xi_i \eta_j p_k | \mathcal{Y}_{ij}^{\xi\eta} \mathcal{E}_k^p | \xi_i \eta_j p_k \rangle - \overset{5}{\leftarrow} \right] \\
&+ \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} (H_i + H_j) \mathcal{E}_i^{\xi} | \xi_i \eta_j \rangle - \overset{1}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k | \mathcal{Y}_{ij}^{\xi\eta} H_k \mathcal{E}_i^{\xi} | \xi_i \eta_j p_k \rangle - \overset{5}{\leftarrow} \\
&+ \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} (H_i + H_j) \mathcal{E}_j^{\eta} | \xi_i \eta_j \rangle - \overset{1}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k | \mathcal{Y}_{ij}^{\xi\eta} H_k \mathcal{E}_j^{\eta} | \xi_i \eta_j p_k \rangle - \overset{5}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k | \mathcal{Y}_{ij}^{\xi\eta} (H_i + H_j + H_k) \mathcal{E}_k^p | \xi_i \eta_j p_k \rangle - \overset{5}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k \sigma_l | \mathcal{Y}_{ij}^{\xi\eta} H_k \mathcal{E}_l^{\sigma} | \xi_i \eta_j p_k \sigma_l \rangle - \overset{23}{\leftarrow} \\
&+ \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} (G_{ij} + G_{ji}) \mathcal{E}_i^{\xi} | \xi_i \eta_j \rangle - \overset{1}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k | \mathcal{Y}_{ij}^{\xi\eta} (G_{ik} + G_{ki} + \\
&\quad + G_{jk} + G_{kj}) \mathcal{E}_i^{\xi} | \xi_i \eta_j p_k \rangle - \overset{5}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k \sigma_l | \mathcal{Y}_{ij}^{\xi\eta} G_{kl} \mathcal{E}_i^{\xi} | \xi_i \eta_j p_k \sigma_l \rangle - \overset{23}{\leftarrow} \\
&+ \langle \xi_i \eta_j | \mathcal{Y}_{ij}^{\xi\eta} (G_{ij} + G_{ji}) \mathcal{E}_j^{\eta} | \xi_i \eta_j \rangle - \overset{1}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k | \mathcal{Y}_{ij}^{\xi\eta} (G_{ik} + G_{ki} + \\
&\quad + G_{jk} + G_{kj}) \mathcal{E}_j^{\eta} | \xi_i \eta_j p_k \rangle - \overset{5}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k \sigma_l | \mathcal{Y}_{ij}^{\xi\eta} G_{kl} \mathcal{E}_j^{\eta} | \xi_i \eta_j p_k \sigma_l \rangle - \overset{23}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k | \mathcal{Y}_{ij}^{\xi\eta} (G_{ik} + G_{ki} + G_{jk} + G_{kj} + \\
&\quad + G_{ij} + G_{ji}) \mathcal{E}_k^p | \xi_i \eta_j p_k \rangle - \overset{5}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k \sigma_l | \mathcal{Y}_{ij}^{\xi\eta} (G_{kl} + G_{lk}) \mathcal{E}_k^p | \xi_i \eta_j p_k \sigma_l \rangle - \overset{23}{\leftarrow} \\
&+ \langle \xi_i \eta_j p_k \sigma_l \tau_m | \mathcal{Y}_{ij}^{\xi\eta} G_{kl} \mathcal{E}_m^{\tau} | \xi_i \eta_j p_k \sigma_l \tau_m \rangle - \overset{119}{\leftarrow}
\end{aligned}$$

APPENDIX B

ORTHONORMALIZATION PROCEDURE

Considerable simplification of the algebra involved in the expansion of the matrix elements can be achieved if the individual one-electron wave functions used to build up the crystal wave function are orthogonal. The simplification occurs because the myriad of overlap terms introduced by antisymmetrization are suppressed by such functions. Of course, these terms appear again when the transformation to atomic functions is made, but in the meanwhile, it has been possible to write out the matrix elements explicitly with a minimum of bookkeeping.

Since we are working in the tight-binding approximation, the most naturally available functions are free atomic ones. However, at the distances of importance these are nonorthogonal and give overlap integrals of the form

$$\Delta_{\mu\nu} = \int \varphi^{\mu*} \varphi^{\nu} d\tau = S_{\mu\nu} + S_{\nu\mu} \quad (\text{B-1})$$

Several methods of orthonormalization are available. Following Knox²⁸ and Gold¹⁸, we shall use the method of symmetric orthonormalization due to Löwdin.^{50,55}

To get an orthonormalized set of functions, ϕ^{μ} ,

we perform a linear transformation on the nonorthogonal set φ^α

$$\phi^\mu = \sum_{\alpha} \varphi^\alpha A_{\alpha\mu} \quad (\text{B-2})$$

and then require that

$$\int \phi^{\mu*} \phi^{\nu} d\tau = \delta_{\mu,\nu}. \quad (\text{B-3})$$

Substituting we get $A^\dagger \Delta A = 1$. This has the solution $A = \Delta^{-1/2} B$ where $B^\dagger B = 1$. Choosing $B = 1$ we have,

$$\phi^\mu = \sum_{\alpha} \varphi^\alpha (1 + S)^{1/2}_{\alpha\mu}. \quad (\text{B-4})$$

This choice of B gives Löwdin's prescription for symmetric orthonormalization. Its value is that it treats all the wave functions on an equivalent basis. Another choice of B would have led to the more familiar Schmidt procedure.

Provided the elements of $S_{\alpha\mu}$ are small so that

$$\sum_{\alpha} |S_{\alpha\alpha}| \leq \eta < 1 \quad (\text{B-5a})$$

the series

$$(1 + S)^{-1/2} = 1 - \frac{1}{2} S + \frac{3}{8} S^2 - \dots \quad (\text{B-5b})$$

converges. Then the orthonormalized wave function is

$$\begin{aligned} \phi^\mu = & \varphi^\mu - \frac{1}{2} \sum_{\alpha} \varphi^\alpha S_{\alpha\mu} \\ & + \frac{3}{8} \sum_{\alpha\beta} \varphi^\alpha S_{\alpha\beta} S_{\beta\mu} - \dots \end{aligned} \quad (\text{B-6})$$

In our particular problem, the sufficient condi-

tion for the convergence of the overlap series is satisfied by the outer shell overlap integrals for the substitutional site. For both the octahedral and tetrahedral interstitial sites, the overlaps are on the borderline. However, for these "cramped" sites, we expect a relaxation of the lattice outwards from the hydrogen impurity, and so these cases would presumably be convergent also.

For this study we shall assume that this series expansion is valid and includes only terms of order S^2 , i.e., we make the " S^2 approximation". A more detailed discussion of convergence is given by Löwdin.⁵⁰

In order to gain a feeling for the convergence of the overlap series, the expansion for the hydrogen "molecule" at various proton separations was investigated. In this case the 2×2 matrix $\Delta^{-1/2}$ can be found analytically for comparison with the series. The results of this comparison are given in Table VIII.

Here we note that even at the normal spacing of $1.4a_0$, the convergence is remarkable considering that the overlap is approximately $3/4$. In this case we would have to use terms of order S^4 or higher to obtain reasonable results. But for our purposes this large overlap is an unreasonable test of the series. A more common value of S for solids of interest would be of order 0.1

TABLE VIII

Convergence Properties of the Löwdin Series for Two Overlapping Hydrogen Atoms

Internuclear distance in a_0	Quantity	Exact	Series up to s^2	Series up to s^3	Series up to s^4	S	% Error in s^2 approx.
1.4 a_0 (normal hydrogen molecule)	A_{11}	1.39	1.21	1.21	1.30	0.754	14.9%
	A_{12}	-0.63	-0.376	-0.51	-0.51		40.4%
3 a_0	A_{11}	1.05 ₁	1.04 ₅	1.04 ₅	1.04 ₉	0.347	0.6%
	A_{12}	-0.189	-0.174	-0.187	-0.187		7.9%
4 a_0	A_{11}	1.01 ₄	1.01 ₄	1.01 ₄	1.01 ₄	0.190	0.0%
	A_{12}	-0.0965	-0.095	-0.097	-0.097		1.6%

or less. For $R = 4a_0$ we have $S = .190$ and even then the S^2 approximation is clearly adequate for most calculations.

It should be noted that this choice of orthonormalization procedure is arbitrary and, as Löwdin points out⁵⁰, it is not a priori evident that the problem of impurity atom properties is best treated by this method. Perhaps successive orthogonalization schemes (the Gram-Schmidt method) or a combination of both successive and symmetric orthonormalization procedures might be more suitable. A calculation using one of these methods would be of interest for comparison with the present work. Gold⁶³ has discussed different orthonormalization methods as applied to the calculation of optical transition energies, but for this problem most of the overlap correction is connected with the excited states.

After a calculation using Löwdin functions has been made, it is necessary to transform back to atomic functions for numerical work. Provided the operator in the matrix elements does not depend on any quantum numbers, for example, if there is no λ^{37} or the like in the operator, matrix multiplication can be used to effect the transformation. Such a case occurs in evaluating the ϵ' 's in equations and where the "zero order" matrix elements are being evaluated.

Here we have to transform $\sum_{\xi} \langle \phi^{\xi} | h | \phi^{\xi} \rangle$.
 Substituting Eq. (B-2) for the ϕ^{ξ} 's, we have

$$\begin{aligned} \sum_{\xi} \langle \phi^{\xi} | h | \phi^{\xi} \rangle &= \\ &= \sum_{\xi} \sum_{\mu} \sum_{\nu} A_{\xi}^{\dagger} \nu (\nu | h | \mu) A_{\mu \xi}, \end{aligned} \quad (\text{B-7})$$

where we have introduced rounded brackets to indicate that the matrix elements are between atomic functions.

Then we write:

$$\sum_{\xi} \langle \phi^{\xi} | h | \phi^{\xi} \rangle = \sum_{\nu} \sum_{\mu} T_{\mu \nu} (\nu | h | \mu), \quad (\text{B-8a})$$

where

$$\sum_{\xi} A_{\mu \xi} A_{\xi}^{\dagger} \nu = T_{\mu \nu} = \delta_{\mu \nu} - P_{\mu \nu}, \quad (\text{B-8b})$$

and

$$\begin{aligned} P_{\mu \nu} &= \\ &= \delta_{\mu \nu} - \sum_{\alpha} S_{\mu \alpha} S_{\alpha \nu} + \sum_{\alpha} \sum_{\beta} S_{\mu \alpha} S_{\alpha \beta} S_{\beta \nu} - \dots \end{aligned} \quad (\text{B-8c})$$

Substituting and collecting terms to order S^2 we have:

$$\begin{aligned} \sum_{\xi} \langle \phi^{\xi} | h | \phi^{\xi} \rangle &= \\ &= \sum_{\nu} (\nu | h | \nu) (1 + \sum_{\alpha} S_{\alpha \nu}^2) \\ &\quad - \sum_{\mu} S_{\mu \nu} (\nu | h | \mu) + \sum_{\alpha} \sum_{\mu \neq \nu} S_{\mu \alpha} S_{\alpha \nu} (\nu | h | \mu). \end{aligned} \quad (\text{B-9})$$

Here we keep terms like $S_{\nu \alpha} S_{\alpha \mu} (\nu | h | \mu)$, $\mu \neq \nu$ since if μ and ν are on the same atom, the matrix element is of order S^0 . If μ and ν are not on the same atom we will consider the matrix element to be of

order S.

On the other hand, when the operator does depend on a quantum number, we cannot sum over ξ as we have done here to form $T_{\mu\nu}$ since the matrix element of an operator depending on ξ taken between states φ^ν and φ^μ is not a constant. In this case we must substitute the explicit series expansion for ϕ^ξ and multiply out the result.

For $\langle \phi^\nu | h(\nu) | \phi^\nu \rangle$ we have:

$$\begin{aligned}
 \langle \phi^\nu | h(\nu) | \phi^\nu \rangle &= \quad \quad \quad (B-10) \\
 &= (\nu | h(\nu) | \nu) \left(1 + \frac{3}{4} \sum_{\alpha} S_{\nu\alpha}^2 \right) \\
 &\quad - \frac{1}{2} \sum_{\alpha} S_{\alpha\nu} [(\nu | h(\nu) | \alpha) + (\alpha | h(\nu) | \nu)] \\
 &\quad + \frac{3}{8} \sum_{\alpha \neq \nu} \sum_{\beta} S_{\alpha\beta} S_{\beta\nu} [(\nu | h(\nu) | \alpha) + (\alpha | h(\nu) | \nu)] \\
 &\quad + \frac{1}{4} \sum_{\alpha} \sum_{\beta} S_{\alpha\nu} S_{\beta\nu} (\alpha | h(\nu) | \beta) .
 \end{aligned}$$

Note that if h did not depend on ν this would lead to the previous result by summing over ν , interchanging the α and ν labels in the first part of the second term and then separating the sum over β into two parts for $\beta = \alpha$ and $\beta \neq \alpha$.

In general we have:

$$\begin{aligned}
 \langle \phi^v | h(v, \mu) | \phi^\mu \rangle &= \\
 &= (v | h(v, \mu) | \mu) \left(1 + \frac{3}{8} \sum_{\alpha} S_{\alpha v}^2 + \frac{3}{8} \sum_{\alpha} S_{\alpha \mu}^2 \right) \quad (\text{B-11}) \\
 &\quad - \frac{1}{2} \sum_{\alpha} S_{\alpha v} (\alpha | h(v, \mu) | \mu) \\
 &\quad - \frac{1}{2} \sum_{\alpha} S_{\alpha \mu} (v | h(v, \mu) | \alpha) \\
 &\quad + \frac{3}{8} \sum_{\alpha \neq v} \sum_{\beta} S_{\alpha \beta} S_{\beta v} (\alpha | h(v, \mu) | \mu) \\
 &\quad + \frac{3}{8} \sum_{\alpha \neq \mu} \sum_{\beta} S_{\alpha \beta} S_{\beta \mu} (v | h(v, \mu) | \alpha) \\
 &\quad + \frac{1}{4} \sum_{\alpha} \sum_{\beta} S_{\alpha v} S_{\beta \mu} (\alpha | h(v, \mu) | \beta)
 \end{aligned}$$

Using Eqs. (B-10) and (B-11) or by direct substitution of the Löwdin series, Eq. (B-9), matrix elements of product wave functions can be evaluated. A table of the transformations follows for both the operator a function of the quantum numbers and the reduced form in which the operator does not depend on the quantum numbers.

h DEPENDENT ON QUANTUM NUMBERS

$$\begin{aligned}
\langle \nu | h(\nu) | \nu \rangle &= (\nu | h(\nu) | \nu) \left(1 + \frac{3}{4} \sum_{\beta} S_{\nu\beta}^2 \right) \\
&\quad - \frac{1}{2} \sum_{\alpha} S_{\nu\alpha} [(\nu | h(\nu) | \alpha) + (\alpha | h(\nu) | \nu)] \\
&\quad + \frac{3}{8} \sum_{\alpha \neq \nu} \sum_{\beta} S_{\alpha\beta} S_{\beta\nu} [(\nu | h(\nu) | \alpha) + (\alpha | h(\nu) | \nu)] \\
&\quad + \frac{1}{4} \sum_{\alpha} \sum_{\beta} S_{\alpha\nu} S_{\beta\nu} (\alpha | h(\nu) | \beta)
\end{aligned}$$

$$\begin{aligned}
\langle \nu | h(\nu\mu) | \mu \rangle &= (\nu | h(\nu\mu) | \mu) \left(1 + \frac{3}{8} \sum_{\alpha} S_{\nu\alpha}^2 + \frac{3}{8} \sum_{\alpha} S_{\alpha\mu}^2 \right) \\
&\quad - \frac{1}{2} \sum_{\alpha} \{ S_{\alpha\nu} (\alpha | h(\nu\mu) | \mu) + S_{\alpha\mu} (\nu | h(\nu\mu) | \alpha) \} \\
&\quad + \frac{3}{8} \sum_{\alpha \neq \nu} \sum_{\beta} S_{\alpha\beta} S_{\beta\nu} (\alpha | h(\nu\mu) | \mu) \\
&\quad \quad + \frac{3}{8} \sum_{\alpha \neq \mu} \sum_{\beta} S_{\alpha\beta} S_{\beta\mu} (\nu | h(\nu\mu) | \alpha) \\
&\quad + \frac{1}{4} \sum_{\alpha} \sum_{\beta} S_{\alpha\nu} S_{\beta\mu} (\alpha | h(\nu\mu) | \beta)
\end{aligned}$$

$$\begin{aligned}
\langle \nu\mu | h(\nu\mu) | \nu\mu \rangle &= \\
&= (\nu\mu | h(\nu\mu) | \nu\mu) \left(1 + \frac{3}{4} \sum_{\alpha} S_{\alpha\nu}^2 + \frac{3}{4} \sum_{\alpha} S_{\alpha\mu}^2 \right) \\
&\quad - \frac{1}{2} \sum_{\alpha} S_{\alpha\nu} [(\nu\mu | h(\nu\mu) | \alpha\mu) + (\alpha\mu | h(\nu\mu) | \nu\mu)] \\
&\quad - \frac{1}{2} \sum_{\alpha} S_{\alpha\mu} [(\nu\mu | h(\nu\mu) | \nu\alpha) + (\nu\alpha | h(\nu\mu) | \nu\mu)] \\
&\quad + \frac{3}{8} \sum_{\alpha \neq \nu} \sum_{\beta} S_{\alpha\beta} S_{\beta\nu} [(\nu\mu | h(\nu\mu) | \alpha\mu) + (\alpha\mu | h(\nu\mu) | \nu\mu)] \\
&\quad + \frac{3}{8} \sum_{\alpha \neq \mu} \sum_{\beta} S_{\alpha\beta} S_{\beta\mu} [(\nu\mu | h(\nu\mu) | \nu\alpha) + (\nu\alpha | h(\nu\mu) | \nu\mu)] \\
&\quad + \frac{1}{4} \sum_{\alpha} \sum_{\beta} \{ S_{\alpha\nu} S_{\beta\mu} [(\nu\mu | h(\nu\mu) | \alpha\beta) + (\alpha\mu | h(\nu\mu) | \nu\beta) \\
&\quad \quad + (\nu\beta | h(\nu\mu) | \alpha\mu) + (\alpha\beta | h(\nu\mu) | \nu\mu)] \\
&\quad + S_{\alpha\nu} S_{\beta\nu} (\alpha\mu | h(\nu\mu) | \beta\mu) \\
&\quad \quad + S_{\alpha\mu} S_{\beta\mu} (\nu\alpha | h(\nu\mu) | \nu\beta) \}
\end{aligned}$$

$$\begin{aligned}
\langle \nu\mu | h(\nu\mu) | \mu\nu \rangle &= \\
&= (\nu\mu | h(\nu\mu) | \mu\nu) \left[1 + \frac{3}{4} \sum_{\alpha} S_{\nu\alpha}^2 + \frac{3}{4} \sum_{\alpha} S_{\mu\alpha}^2 \right] \\
&\quad - \frac{1}{2} \sum_{\alpha} S_{\alpha\nu} [(\nu\mu | h(\nu\mu) | \mu\alpha) + (\alpha\mu | h(\nu\mu) | \mu\nu)] \\
&\quad - \frac{1}{2} \sum_{\alpha} S_{\alpha\mu} [(\nu\mu | h(\nu\mu) | \alpha\nu) + (\nu\alpha | h(\nu\mu) | \mu\nu)] \\
&\quad + \frac{3}{8} \sum_{\alpha \neq \beta} S_{\alpha\beta} S_{\beta\nu} [(\nu\mu | h(\nu\mu) | \mu\alpha) + (\alpha\mu | h(\nu\mu) | \mu\nu)] \\
&\quad + \frac{3}{8} \sum_{\alpha \neq \mu} S_{\alpha\beta} S_{\beta\mu} [(\nu\mu | h(\nu\mu) | \alpha\nu) + (\nu\alpha | h(\nu\mu) | \mu\nu)] \\
&\quad + \frac{1}{4} \sum_{\alpha} \sum_{\beta} \{ S_{\alpha\mu} S_{\beta\nu} [(\nu\mu | h(\nu\mu) | \alpha\beta) + (\beta\mu | h(\nu\mu) | \alpha\nu) \\
&\quad \quad + (\nu\alpha | h(\nu\mu) | \mu\beta) + (\beta\alpha | h(\nu\mu) | \mu\nu)] \\
&\quad \quad + S_{\alpha\nu} S_{\beta\nu} (\alpha\mu | h(\nu\mu) | \mu\beta) \\
&\quad \quad + S_{\alpha\mu} S_{\beta\mu} (\nu\alpha | h(\nu\mu) | \beta\nu) \}
\end{aligned}$$

h INDEPENDENT OF QUANTUM NUMBERS

$$\begin{aligned} \sum_{\xi} \langle \xi | h | \xi \rangle &= \sum_{\nu} (\nu | h | \nu) \left(1 + \sum_{\alpha} S_{\alpha \nu}^2 \right) \\ &\quad - \sum_{\mu \nu} (\nu | h | \mu) \\ &\quad + \sum_{\alpha} \sum_{\mu \neq \nu} S_{\mu \alpha} S_{\alpha \nu} (\nu | h | \mu) \end{aligned}$$

$$\begin{aligned} \sum_{\xi} \sum_{\eta} \langle \xi \eta | h | \xi \eta \rangle &= \\ &= \sum_{\nu} \sum_{\mu} (\nu \mu | h | \nu \mu) \left(1 + \sum_{\alpha} S_{\nu \alpha}^2 + \sum_{\alpha} S_{\mu \alpha}^2 \right) \\ &\quad - \sum_{\alpha} S_{\alpha \nu} (\nu \mu | h | \alpha \mu) \\ &\quad - \sum_{\alpha} S_{\alpha \mu} (\nu \mu | h | \nu \alpha) \\ &\quad + \sum_{\alpha} \sum_{\substack{\beta \\ \alpha \neq \mu}} S_{\alpha \beta} S_{\beta \mu} (\nu \mu | h | \nu \alpha) \\ &\quad + \sum_{\alpha} \sum_{\substack{\beta \\ \alpha \neq \nu}} S_{\alpha \beta} S_{\beta \nu} (\nu \mu | h | \alpha \mu) \\ &\quad + \sum_{\alpha} \sum_{\beta} S_{\alpha \nu} S_{\beta \mu} (\nu \mu | h | \alpha \beta) \end{aligned}$$

$$\begin{aligned} \sum_{\xi} \sum_{\eta} \langle \xi \eta | h | \eta \xi \rangle &= \\ &= \sum_{\nu} \sum_{\mu} (\nu \mu | h | \mu \nu) \left(1 + \sum_{\alpha} S_{\nu \alpha}^2 + \sum_{\alpha} S_{\mu \alpha}^2 \right) \\ &\quad - \sum_{\alpha} S_{\alpha \nu} (\nu \mu | h | \mu \alpha) \\ &\quad - \sum_{\alpha} S_{\alpha \mu} (\nu \mu | h | \alpha \nu) \\ &\quad + \sum_{\alpha} \sum_{\substack{\beta \\ \alpha \neq \mu}} S_{\alpha \beta} S_{\beta \mu} (\nu \mu | h | \alpha \nu) \\ &\quad + \sum_{\alpha} \sum_{\substack{\beta \\ \alpha \neq \nu}} S_{\alpha \beta} S_{\beta \nu} (\nu \mu | h | \mu \alpha) \\ &\quad + \sum_{\alpha} \sum_{\beta} S_{\alpha \nu} S_{\beta \mu} (\nu \mu | h | \beta \alpha) \end{aligned}$$

APPENDIX C

DETAILS OF THE CALCULATION OF THE VARIATIONAL PARAMETERS

1. The Crystal Field Parameters, Λ^ξ a. The crystal field energy

The contribution to the energy involving Λ 's is

$$\begin{aligned}
 E_{\Lambda} = & \sum_{\xi} 2 I_{\xi} \Lambda^{\xi} + \sum_{\xi} \sum_{\eta} J_{\xi\eta} \Lambda^{\xi} \Lambda^{\eta} \\
 & + \sum_{\xi} \sum_{\eta} 2 K_{\xi\eta} \Lambda^{\xi} L^{\eta} \\
 & + \sum_{\xi} \sum_{\eta} \sum_{\rho \neq \eta} 2 L_{\xi,\eta\rho} \Lambda^{\xi} \lambda^{\eta\rho}.
 \end{aligned}
 \tag{C-1}$$

From Eq. (7-4) these terms are

$$\sum_{\xi} 2 I_{\xi} \Lambda^{\xi} = 2 [\langle u_1 | \mathcal{H}' | u_0 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_1 | u_0 \rangle] \tag{C-2a}$$

$$\begin{aligned}
 \sum_{\xi} \sum_{\eta} J_{\xi\eta} \Lambda^{\xi} \Lambda^{\eta} = & \\
 = & \langle u_1 | \mathcal{H}' | u_1 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_1 | u_1 \rangle \\
 & - 4 \langle u_1 | u_0 \rangle \cdot \\
 & \cdot [\langle u_1 | \mathcal{H}' | u_0 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_1 | u_0 \rangle]
 \end{aligned}
 \tag{C-2b}$$

$$\begin{aligned}
\sum_{\xi} \sum_{\eta} 2 K_{\xi \eta} \Lambda^{\xi} \mathcal{L}^{\eta} &= \\
&= \langle u_1 | \mathcal{H}' | u_2 \rangle + \langle u_2 | \mathcal{H}' | u_1 \rangle \\
&\quad - \langle u_0 | \mathcal{H}' | u_0 \rangle [\langle u_1 | u_2 \rangle + \langle u_2 | u_1 \rangle] \\
&\quad - 2 \langle u_1 | u_0 \rangle [\langle u_0 | \mathcal{H}' | u_2 \rangle + \langle u_2 | \mathcal{H}' | u_0 \rangle] \\
&\quad - 2 \langle u_1 | \mathcal{H}' | u_0 \rangle [\langle u_2 | u_0 \rangle + \langle u_0 | u_2 \rangle] \\
&\quad + 4 \langle u_1 | u_0 \rangle [\langle u_2 | u_0 \rangle + \langle u_0 | u_2 \rangle] \langle u_0 | \mathcal{H}' | u_0 \rangle
\end{aligned}
\tag{C-2c}$$

$$\begin{aligned}
\sum_{\xi} \sum_{\eta} \sum_{\rho} 2 L_{\xi, \eta \rho} \Lambda^{\xi} \chi^{\eta \rho} &= 2 [\langle u_1 | \mathcal{H}' | u_3 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_1 | u_3 \rangle] \\
&\quad - 4 [\langle u_1 | u_0 \rangle \langle u_0 | \mathcal{H}' | u_3 \rangle \\
&\quad + \langle u_1 | \mathcal{H}' | u_0 \rangle \langle u_0 | u_3 \rangle \\
&\quad - 2 \langle u_1 | u_0 \rangle \langle u_0 | u_3 \rangle \langle u_0 | \mathcal{H}' | u_0 \rangle].
\end{aligned}
\tag{C-2d}$$

Here we have combined the two terms $\langle u_1 | \mathcal{H}' | u_0 \rangle$ and $\langle u_0 | \mathcal{H}' | u_1 \rangle$ to give $2 \langle u_1 | \mathcal{H}' | u_0 \rangle$. This is allowed since u_1 is formed from u_0 by a simple multiplication (see Eq. (6-6)). This also holds for matrix elements

involving u_3 . In the case of u_2 , the operator $\underline{L} \cdot \underline{\sigma}$ is involved and we have written these terms out in full since the two may be different. For example, using the spin-orbit term of the Hamiltonian we have two possibilities

$$\langle \xi | \omega^\xi \underline{L} \cdot \underline{\sigma} (\underline{L} \cdot \underline{\sigma}) | \xi \rangle \quad \text{or} \quad \langle \xi | \underline{L} \cdot \underline{\sigma} (\omega^\xi \underline{L} \cdot \underline{\sigma}) | \xi \rangle.$$

Provided ω^ξ is an s function these are the same. We shall make this choice for ω^ξ , but prefer not to make this assumption yet.

The Λ^ξ corresponding to minimum energy is

$$\Lambda^\xi = -\frac{I_\xi}{J_{\xi\xi}} - \frac{\sum_{\gamma \neq \xi} \frac{1}{2} (J_{\xi\gamma} + J_{\gamma\xi}) \Lambda^\gamma + \sum_{\gamma \neq \xi} K_{\xi\gamma} \mathcal{L}^\gamma + \sum_{\gamma \neq \xi} \frac{L_{\xi,\gamma\rho} (\lambda^\rho + \lambda^\gamma)}{J_{\xi\xi}}}{J_{\xi\xi}} \quad (C-3)$$

Here we have combined the $\lambda^{\xi\gamma}$ and the $\lambda^{\gamma\xi}$ terms since the two parameters are strongly coupled and only their sum has meaning.

b. The I_ξ term

Using the expansion $\mathcal{H}' = \omega + \sum_i H_i + \sum_{i,j}' G_{ij}$ and substituting in Eq. (C-2a) we have

$$I_{\xi} = \langle \xi | v^{\xi} H | \xi \rangle + \sum_{\eta \neq \xi} \langle \xi | \eta | v^{\xi} G_{ij} | \xi | \eta \rangle - \langle \xi | \eta | v^{\xi} G_{ij} | \xi | \eta \rangle - \langle \xi | v^{\xi} | \xi \rangle.$$

$$\begin{aligned} & [\langle \xi | H | \xi \rangle + \sum_{\eta \neq \xi} \langle \xi | \eta | G_{ij} | \xi | \eta \rangle - \langle \xi | \eta | G_{ij} | \eta | \xi \rangle] \\ & - \sum_{\eta \neq \xi} \langle \xi | v^{\xi} | \eta \rangle. \\ & [\langle \eta | H | \xi \rangle + \sum_{\substack{\rho \neq \xi \\ \rho \neq \eta}} \langle \eta | \rho | G_{ij} | \xi | \rho \rangle - \langle \eta | \rho | G_{ij} | \rho | \xi \rangle] \end{aligned} \quad (C-4)$$

This must now be expanded according to Appendix A to get the matrix elements in terms of atomic functions. However, since we are mainly concerned with the impurity atom, we need only consider the case for ξ , the 1s hydrogen state. Then we will profit from the fact that since the hydrogen atom has only one electron, all exchange terms involving ξ are between electrons on different atoms and so are of order s^2 .

Further simplification becomes apparent on considering the direct terms. They are

$$\begin{aligned} I_{\xi \text{ Direct}} &= \\ &= (\xi | v^{\xi} H | \xi) + \sum_{\eta \neq \xi} (\xi | \eta | v^{\xi} G_{ij} | \xi | \eta) \\ &\quad - (\xi | v^{\xi} | \xi) \left[(\xi | H | \xi) + \sum_{\eta \neq \xi} (\xi | \eta | G_{ij} | \xi | \eta) \right]. \end{aligned} \quad (C-5)$$

On substituting for the terms of the Hamiltonian, the energy eigenvalues for state φ^{ξ} cancel and we are left with

$$I_{\xi} \text{ Direct} = (\xi | \sum' V_{\xi} | \xi) - (\xi | \sum' V_{\xi} | \xi) (\xi | \sum' V_{\xi} | \xi), \quad (C-5')$$

$$\text{where } \sum' V_{\xi} (r_i) = e^2 \left[\sum_J^* \frac{z_J}{|r_i - R_J|} + \sum_{\eta \neq \xi}^* (\eta_j | \frac{1}{r_{ij}} | \eta_j) \right].$$

In this definition the * on the sums indicates that the summation is to run over all atoms except the one on which φ^{ξ} is centered. Thus, if φ^{ξ} is centered on nucleus "I" the first sum is $\sum_J^* = \sum_{J \neq I}$, and the second sum excludes those values of η for which φ^{η} is centered on nucleus I.

Clearly $\sum' V_{\xi} (r_i)$ is just the sum of the potentials of the atoms making up the crystal less that of the atom on which φ^{ξ} is centered. In a molecular crystal these atomic potentials are well localized as the "internal" fields of the atoms. Consequently for $(\xi | \sum' V_{\xi} | \xi)$ or similar matrix elements to be non-zero, wave function φ^{ξ} must overlap the wave functions of neighboring atoms. Hence it seems reasonable to consider that $I_{\xi} \text{ Direct}$ of Eq. (C-5') is proportional to some power of S.

A graph of $(\varphi^{H,1s}(r_i) | V_{\text{Argon}}(r_i) | \varphi^{H,1s}(r_i))$, where $\varphi^{H,1s}$

Fig. 8. Comparison of hydrogen-argon overlap with the matrix elements of the argon self-consistent potential.

is the hydrogen 1s function, for various argon-hydrogen internuclear distances is given in Fig. 8. Here Hartree's self-consistent potential for neutral argon has been used for V_{argon} . On the same graph are plotted $S_{\text{A3p,H1s}}$, the argon 3p, hydrogen 1s overlap and its square. From this it seems that the matrix element is nearly proportional to $S_{\text{A3p,H1s}}^2$, presumably the behavior of $(\psi^{\text{H,1s}} | \psi^{\text{H,1s}} V_{\text{Argon}} | \psi^{\text{H,1s}})$ will be similar, and in this sense we shall take such matrix elements to be of order S^2 in molecular crystals.

Using the equations given in Appendix B, Eq.(C-4) may be expanded. To order S^2 the terms in energy eigenfunctions cancel identically and terms involving expectation values of crystal field potentials times overlap integrals are of order greater than S^2 by the argument of the preceding paragraph. The final result is

$$\begin{aligned}
 I_0 = & (0 | \psi^0 \tilde{\Sigma}' V_0 | 0) - \sum_{\eta} (0 | \psi^0 | \eta) (\eta | \tilde{\Sigma}' V_0 | 0) \\
 & - \frac{1}{2} \sum_{\alpha} S_{0\alpha} \left\{ (0 | \psi^0 \tilde{\Sigma}' V_{\alpha} | \alpha) + (\alpha | \psi^0 \tilde{\Sigma}' V_0 | 0) \right. \\
 & \quad \left. - (0 | \psi^0 | 0) [(0 | \tilde{\Sigma}' V_{\alpha} | \alpha) + 2(\alpha | \tilde{\Sigma}' V_0 | 0)] \right\} \\
 & - \frac{1}{2} \sum_{\alpha} S_{0\alpha} \sum_{\eta \neq 0} \left\{ (0 | \psi^0 / r_{0j} | 0 \eta) - (0 | \psi^0 / r_{0j} | \eta 0) \right. \\
 & \quad \left. - (0 | \psi^0 | 0) \cdot \right. \\
 & \quad \left. [(0 | \psi^0 / r_{0j} | 0 \eta) - (0 | \psi^0 / r_{0j} | \eta 0)] \right\} \quad (C-6)
 \end{aligned}$$

Here the notation "0" represents $\xi = 0$ = hydrogen 1s function. The potential $\tilde{\Sigma}' V_{\xi}$ is shorthand for the exchange potential defined by

$$\begin{aligned} \tilde{\Sigma}' V_{\xi} (\chi_i) | \varphi^{\xi} \rangle &= \quad (C-7) \\ &= e^2 \left[- \sum_{J'}^* \frac{Z_{J'}}{|\chi_i - R_{J'}|} | \varphi^{\xi} \rangle \right. \\ &\quad \left. + \sum_{\eta \neq \xi}^* (\chi_j | \frac{1}{r_{ij}} | \chi_j) | \varphi^{\xi} \rangle - (\chi_j | \frac{1}{r_{ij}} | \xi_j) | \varphi^{\eta} \rangle \right]. \end{aligned}$$

The first line of (C-6) is just the "zero order" term in the Löwdin expansion. The second line and two of the terms in the third line result from replacing ϕ^0 in the bra or ket of the terms $\langle 0 | v^0 \chi | 0 \rangle$ and $\langle 0 | \chi | 0 \rangle$ with $\phi^0 = \varphi^0 - \frac{1}{2} \sum_{\alpha} S_{0\alpha} \varphi^{\alpha} + \dots$. The third term in line 3, $(\chi | \tilde{\Sigma}' V_0 | 0)$, comes from replacing ϕ^{η} with $\phi^{\eta} = \varphi^{\eta} - \frac{1}{2} S_{\eta 0} \varphi^0$ in the first matrix element of $\sum_{\eta} \langle 0 | v^0 | \eta \rangle \langle \eta | \tilde{\Sigma}' V_0 | 0 \rangle$.

The third and fourth lines result from the terms

$$\begin{aligned} \sum_{\eta \neq 0} \langle 0 | \chi_j | v^0 / r_{ij} | 0 | \chi_j \rangle &- \langle 0 | \chi_j | v^0 / r_{ij} | \chi_i 0 \rangle \\ &- \langle 0 | v^0 | 0 \rangle. \end{aligned}$$

$$\left[\sum_{\eta \neq 0} \langle 0 | \chi_j | 1/r_{ij} | 0 | \chi_j \rangle - \langle 0 | \chi_j | 1/r_{ij} | \chi_i 0 \rangle \right]$$

when ϕ^{η} is expanded in the bra. Expansion of ϕ^{η} in the ket gives nothing since the resulting terms cancel identically.

The potential, $\sum' V_{\xi}$, needs some explanation. The first two terms represent the Hartree self-consistent potential of an atom as seen by an electron whose wave function overlaps the atom. The third term is the exchange energy. We have shown that the sum of the first two terms leads to matrix elements of order S^2 . The exchange term, although a correction, is also of order S^2 since the term $(\xi|\eta| \frac{1}{r_{ij}} |\eta|\xi)$ represents the electrostatic interaction between "charge clouds" of density $\varphi^{\xi*} \varphi^{\eta}$ and $\varphi^{\eta*} \varphi^{\xi}$. For φ^{ξ} and φ^{η} on different atoms these clouds are of order S in density, but they are "on top of one another" so their interaction should be included in an S^2 calculation.

c. The $J_{\xi\eta}$ terms

Since we seek to find the impurity wave function correct to order S^2 , we must find Λ to order S^2 . The leading term in I_{ξ} is itself proportional to S^2 so we need to find $J_{\xi\xi}$ to order S^0 . Furthermore, since the cross terms are "second generation" effects we only consider S^0 terms and so need $J_{\xi\eta}$ to order S^0 also.

In finding the J terms we shall divide their contribution to the energy into two parts

$$\sum_{\xi} \sum_{\eta} J_{\xi\eta} \Lambda^{\xi} \Lambda^{\eta} = J_1 + J_2 \quad (C-8)$$

where

$$J_1 = \langle u_1 | \mathcal{H}' | u_1 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_1 | u_1 \rangle$$

$$J_2 = 4 \langle u_1 | u_0 \rangle [\langle u_1 | \mathcal{H}' | u_0 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_1 | u_0 \rangle].$$

Keeping just the S^0 terms J_1 may be written directly from Eq. (C-2b) and the formulas for expansion of the u 's in Appendix A. The terms in W cancel leaving

$$\begin{aligned} J_1 = \sum_{\xi} \Lambda^{\xi^2} \{ & (\xi_i | v_i^{\xi} [H_i + \sum_{j \neq \xi} (\eta_j | 2G_{ij} | \eta_j)] v_i^{\xi} | \xi_i) \\ & - (\xi_i | v^{\xi^2} | \xi_i) \\ & (\xi_i | H_i + \sum_{j \neq \xi} (\eta_j | 2G_{ij} | \eta_j) | \xi_i) \} \\ & + \sum_{\xi} \sum_{j \neq \xi} \Lambda^{\xi} \Lambda^j \{ (\xi_i | \eta_j | v_i^{\xi} [H_i + H_j + 2G_{ij} \\ & + \sum_{\substack{p \neq \xi \\ \neq j}} (p_k | 2G_{ik} | p_k) \\ & + (p_k | 2G_{jk} | p_k)] v_j^{\eta} | \xi_i | \eta_j) \\ & - (\xi_i | \eta_j | v_i^{\xi} v_j^{\eta} | \xi_i | \eta_j) \\ & [(\xi_i | H_i + (\eta_j | G_{ij} | \eta_j) + \sum_{\substack{p \neq \xi \\ \neq j}} (p_j | 2G_{ij} | p_j) | \xi_i) \\ & + (\xi_j | H_j + (\xi_i | G_{ij} | \xi_i) + \sum_{\substack{p \neq \xi \\ \neq j}} (p_i | 2G_{ij} | p_i) | \eta_j)] \} \end{aligned} \quad (C-9)$$

Now, consider the first integral

$$T = (\xi_i | v_i^{\xi} [H_i + 2 \sum_{j \neq \xi} (\eta_j | G_{ij} | \eta_j)] v_i^{\xi} | \xi_i). \quad (C-10)$$

Ignoring the spin-orbit term, which is small compared to the other interaction, we can divide the operator into atomic and "crystal field" terms

$$T = (\xi_i | v_i^\xi \left[-\frac{1}{2} \nabla_i^2 - \frac{Z_I}{r_{iI}} + \sum_{\substack{\eta \neq \xi \\ \eta \text{ on the same} \\ \text{center}}} (\eta_j | \frac{1}{r_{ij}} | \eta_j) + \sum' \frac{1}{r_{\xi}} \right] v_i^\xi | \xi_i) \quad (C-11)$$

now

$$\begin{aligned} \nabla^2 (v^\xi \varphi^\xi) &= \\ &= v^\xi \nabla^2 \varphi^\xi + 2(\underline{\nabla} v^\xi) \cdot (\underline{\nabla} \varphi^\xi) + \varphi^\xi (\nabla^2 v^\xi) \end{aligned} \quad (C-12)$$

and furthermore,

$$\begin{aligned} (\xi | v^\xi \underline{\nabla} v^\xi \cdot \underline{\nabla} \varphi^\xi | \xi) + (\xi | v^\xi (\nabla^2 v^\xi) \varphi^\xi | \xi) & \quad (C-12') \\ &= -(\xi | \underline{\nabla} v^\xi \cdot \underline{\nabla} v^\xi | \xi), \end{aligned}$$

which follows on integrating the second term by parts and setting the surface integral at infinity equal to zero. Combining these,

$$\begin{aligned} T &= \epsilon_\xi (\xi | v^{\xi 2} | \xi) & (C-13) \\ &+ \frac{1}{2} (\xi | \underline{\nabla} v^\xi \cdot \underline{\nabla} v^\xi | \xi) + (\xi | v^\xi \sum' \frac{1}{r_{\xi}} v^\xi | \xi) \end{aligned}$$

where ϵ_ξ is the energy eigenvalue for the atomic state φ^ξ .

The $\wedge^\xi \wedge^\eta$ term poses a different problem, how-

ever. The Hamiltonian operator may be thought of as operating to the right on coordinate i and to the left on coordinate j . Hence no additional terms are introduced by the differential operator as above. However, the potential part must be broken up differently because of the G_{ij} term. We can rewrite

$$H_i + H_j + 2G_{ij} + \sum_{\substack{p \neq \xi \\ p \neq \eta}} (p_k | 2G_{ik} | p_k) \\ + \sum_{\substack{p \neq \xi \\ p \neq \eta}} (p_k | 2G_{jk} | p_k)$$

symbolically as

$$H_0(\underline{r}_i) + H_0(\underline{r}_j) + 2G_{ij} + \sum' V_{\xi}(\underline{r}_i) - (\eta_k | 2G_{ik} | \eta_k) + \\ + \sum' V_{\eta}(\underline{r}_j) - (\xi_k | 2G_{jk} | \xi_k), \quad (C-14)$$

where $H_0(\underline{r}_i)$ is the atomic Hamiltonian.

Using the notation

$$\sum'' V_{\xi;\eta}(\underline{r}_i) = \\ = \sum' V_{\xi}(\underline{r}_i) - (\eta_k | 2G_{ik} | \eta_k), \quad (C-15)$$

we get on substituting (C-13) and (C-14) into the equation for J_1 ,

$$J_1 = \sum_{\xi} \Lambda_{\xi}^2 \left\{ \frac{1}{2} (\xi | \underline{\nabla} v^{\xi} \cdot \underline{\nabla} v^{\xi} | \xi) \right. \\ \left. + (\xi | v^{\xi^2} \sum' V_{\xi} | \xi) - (\xi | v^{\xi^2} | \xi) (\xi | \sum' V_{\xi} | \xi) \right\}$$

$$\begin{aligned}
& + \sum_{\xi} \sum_{\eta \neq \xi} \Lambda^{\xi} \Lambda^{\eta} \left\{ (\xi_i \eta_j | v_i^{\xi} (\sum_{\xi'} V_{\xi'\eta}(\underline{r}_i) + \sum_{\eta'} V_{\eta'\xi}(\underline{r}_j) + \frac{1}{r_{ij}}) v_j^{\eta} | \xi_i \eta_j) \right. \\
& \quad \left. - (\xi_i \eta_j | v_i^{\xi} v_j^{\eta} | \xi_i \eta_j) \right. \\
& \quad \left[(\xi | \sum_{\eta} V_{\eta\xi}(\underline{r}_i) | \xi) + (\eta | \sum_{\xi} V_{\xi\eta}(\underline{r}_j) \right. \\
& \quad \left. + (\xi_i \eta_j | \frac{1}{r_{ij}} | \xi_i \eta_j) \right] \left. \right\}. \quad (C-16)
\end{aligned}$$

The second part of J is from our previous work

$$J_2 = 4 \sum_{\xi} \sum_{\eta \neq \xi} \Lambda^{\xi} \Lambda^{\eta} (\xi | v^{\xi} | \xi) I_{\eta}. \quad (C-17)$$

We have shown that matrix elements of the crystal field are of order S^2 , so to find J to order S^0 we therefore drop all terms involving the crystal field. In doing this we must pay special attention to the $\Lambda^{\xi} \Lambda^{\eta}$ term when ξ and η are on the same atom. In this case, we are dealing with differences of matrix elements involving $1/r_{ij}$ where $\underline{r}_i$ and $\underline{r}_j$ are on the same atom which cannot be neglected, whereas when $\underline{r}_i$ and $\underline{r}_j$ are on different atoms this interaction is lumped into the "crystal field" which is of order S^2 .

Hence we have to order S^0

$$J = \sum_{\xi} \Lambda^{\xi^2} (\xi | \underline{\nabla} v^{\xi} \cdot \underline{\nabla} v^{\xi} | \xi) +$$

$$\begin{aligned}
& + \sum_{\xi} \sum_{\eta \neq \xi} \wedge^{\xi} \wedge^{\eta} \left\{ (\xi_i \eta_j | v_i^{\xi} \left[\frac{1}{r_{ij}} - \right. \right. \\
& \quad \left. \left. - (\eta_k | \frac{1}{r_{ik}} | \eta_k) - (\xi_k | \frac{1}{r_{jk}} | \xi_k) \right] v_j^{\eta} | \xi_i \eta_j) \right. \\
& \quad \left. - (\xi_i \eta_j | v_i^{\xi} v_j^{\eta} | \xi_i \eta_j) \cdot \right. \\
& \quad \left. \cdot (\xi_i \eta_j | \frac{1}{r_{ij}} | \xi_i \eta_j) \right\}.
\end{aligned} \tag{C-18}$$

From this we have

$$J_{\xi\xi} = \frac{1}{2} (\xi | \nabla v^{\xi} \cdot \nabla v^{\xi} | \xi) \tag{C-19}$$

and

$$J_{\xi\eta} = 0 \quad \text{if } \xi \text{ and } \eta \text{ are on different atoms}$$

$$\begin{aligned}
& = (\xi_i \eta_j | v_i^{\xi} \left[\frac{1}{r_{ij}} - (\eta_k | \frac{1}{r_{ik}} | \eta_k) - \right. \\
& \quad \left. - (\xi_k | \frac{1}{r_{jk}} | \xi_k) \right] v_j^{\eta} | \xi_i \eta_j) - \\
& \quad - (\xi_i \eta_j | v_i^{\xi} v_j^{\eta} | \xi_i \eta_j) (\xi_i \eta_j | \frac{1}{r_{ij}} | \xi_i \eta_j) \\
& \quad \text{if } \xi \text{ and } \eta \text{ are on the same atom.}
\end{aligned}$$

d. The $K_{\xi\eta}$ term

To evaluate this term we notice that in deriving the I_{ξ} terms to "order S^0 " we could have used as the Hamiltonian the one-electron operator atomic Hamiltonian plus crystal field. Symbolically,

$$\mathcal{H}' \approx \sum_i \mathcal{H}_0(\mathbf{r}_i) + \mathcal{H}_{s.o.}(\mathbf{r}_i) + \sum' V(\mathbf{r}_i) \quad (\text{C-20})$$

where we have included the spin-orbit term, $\mathcal{H}_{s.o.}$, explicitly.

From Eq. (C-2c) and Appendix B we have

$$\begin{aligned} \sum_{\xi} \sum_{\eta} K_{\xi\eta} \Lambda^{\xi} \mathcal{L}^{\eta} &= \quad \quad \quad (\text{C-21}) \\ &= \sum_{\xi} \Lambda^{\xi} \mathcal{L}^{\xi} \left\{ \frac{1}{2} (\xi | \nabla \mathbf{v}^{\xi} \cdot \nabla \omega^{\xi} (\mathbf{L} \cdot \boldsymbol{\sigma}) | \xi) + \right. \\ &\quad \left. + (\xi | \mathbf{v}^{\xi} \omega^{\xi} \mathbf{L} \cdot \boldsymbol{\sigma} (H_0 + \mathcal{H}_{s.o.} + \sum' V_{\xi}) | \xi) \right\} - \\ &\quad - \sum_{\xi} \sum_{\eta} \Lambda^{\xi} \mathcal{L}^{\eta} (\xi | \mathbf{v}^{\xi} \omega^{\xi} \mathbf{L} \cdot \boldsymbol{\sigma} | \eta) (\eta | H_0 + \mathcal{H}_{s.o.} + \sum' V_{\xi} | \xi) \\ &\quad - \sum_{\xi} \sum_{\eta} \Lambda^{\xi} \mathcal{L}^{\xi} [(\xi | \mathbf{v}^{\xi} | \eta) (\eta | [H_0 + \mathcal{H}_{s.o.} + \sum' V_{\xi}] \omega^{\xi} \mathbf{L} \cdot \boldsymbol{\sigma} | \xi) + \\ &\quad + (\xi | \mathbf{v}^{\xi} (H_0 + \mathcal{H}_{s.o.} + \sum' V_{\xi}) | \eta) (\eta | \omega^{\xi} \mathbf{L} \cdot \boldsymbol{\sigma} | \xi)] \\ &\quad + \sum_{\xi} \sum_{\eta} \sum_{\rho} \Lambda^{\xi} \mathcal{L}^{\xi} (\xi | \mathbf{v}^{\xi} | \rho) (\eta | \omega^{\xi} \mathbf{L} \cdot \boldsymbol{\sigma} | \xi) \cdot \\ &\quad \cdot (\rho | H_0 + \mathcal{H}_{s.o.} + \sum' V_{\eta} | \eta) \\ &\quad + \Lambda^{\xi} \mathcal{L}^{\rho} (\xi | \mathbf{v}^{\xi} | \eta) (\eta | \omega^{\rho} \mathbf{L} \cdot \boldsymbol{\sigma} | \rho) \cdot \\ &\quad \cdot (\rho | H_0 + \mathcal{H}_{s.o.} + \sum' V_{\xi} | \xi) . \end{aligned}$$

In deriving this we have treated the first term,

$$\langle \xi | \mathbf{v}^{\xi} \mathcal{H}' \omega^{\xi} \mathbf{L} \cdot \boldsymbol{\sigma} | \xi \rangle + \langle \xi | \omega^{\xi} \mathbf{L} \cdot \boldsymbol{\sigma} \mathcal{H}' \mathbf{v}^{\xi} | \xi \rangle$$

as we did the first term in J_1 (see Eqs. (C-10) through (C-13)). We have also assumed that $\mathbf{v}^{\xi}(\mathbf{r}_i)$ and $\omega^{\xi}(\mathbf{r}_i)$ are s-like functions. This last assumption eliminates terms

involving $\underline{L} v^{\xi}$ and $\underline{L} \omega^{\xi}$.

Since we are interested in the sum $\sum_{\eta} K_{\xi\eta} \mathcal{L}^{\eta}$ where φ^{ξ} is the hydrogen 1s function, the first six terms are zero by $\underline{L} \varphi^{\xi} = 0$. The seventh term is of order at least S^2 and in any event, the sum over η and ρ will cause $\langle \eta | \omega^{\rho} \underline{L} \cdot \underline{\sigma} | \rho \rangle$ to sum to zero, since we sum over all ℓ_m 's as η and ρ run over the closed argon shells.

The cross terms with $\mathcal{L}^{\eta}$ therefore make no contribution to Λ^{ξ} .

e. The $L_{\xi, \eta\rho}$ terms

Since this term involves the function $u_{ij}^{\xi\eta}$ approximating the Hamiltonian by (C-20) would suppress terms involving electron correlation or 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 Brooks⁶⁴ one would presume that the dipole-dipole term would be sufficient to estimate the correction. Thus we shall use

$$\mathcal{H}' \approx \sum_i \mathcal{H}_0(\underline{r}_i) + \frac{1}{2} \sum_{i,j}' v_{ij}, \quad (C-22)$$

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 $\underline{r}_i$ and $\underline{r}_j$ be coordinates of functions centered on different atoms.

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

$$\begin{aligned} \sum_{\xi} \sum_{\eta < \rho} \sum_{\rho} 2 L_{\xi, \eta \rho} \Lambda^{\xi} (\lambda^{\eta \rho} + \lambda^{\rho \eta}) &= \quad (C-23) \\ &= 2 \langle u_1 | \mathcal{H}' | u_3 \rangle - 2 \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_1 | u_3 \rangle - \\ &\quad - 4 \langle u_1 | u_0 \rangle \langle u_0 | \mathcal{H}' | u_3 \rangle - 4 \langle u_3 | u_0 \rangle \langle u_0 | \mathcal{H}' | u_1 \rangle \\ &\quad + 8 \langle u_1 | u_0 \rangle \langle u_0 | u_3 \rangle \langle u_0 | \mathcal{H}' | u_0 \rangle. \end{aligned}$$

The free atomic energy eigenvalues, ϵ_v , will cancel in the first two terms except for the " $\underline{v}$ " term in the matrix element $\langle u_1 | \mathcal{H}' | u_3 \rangle$. The ϵ_v '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 are

$$\begin{aligned} \sum_{\xi} \sum_{\eta < \rho} \sum_{\rho} 2 L_{\xi, \eta \rho} \Lambda^{\xi} (\lambda^{\eta \rho} + \lambda^{\rho \eta}) & \quad (C-24) \\ &= 2 \langle u_1 | v_{ij} | u_3 \rangle - 4 \langle u_1 | u_0 \rangle \langle u_3 | u_0 \rangle. \end{aligned}$$

The " ∇ " term may be written down in analogy with Eqs. (C-13) and (C-21) of Sections 1.d and 1.e of this Appendix. The result is

$$\begin{aligned} \sum_{\xi < \eta} \Lambda^{\xi} (\lambda^{\xi\eta} + \lambda^{\eta\xi}) (\xi; \eta_j | \sum_i u_{ij}^{\xi\eta} \cdot \sum_i v_i^{\xi} | \xi; \eta_j) \\ + \Lambda^{\eta} (\lambda^{\xi\eta} + \lambda^{\eta\xi}) (\xi; \eta_j | \sum_j u_{ij}^{\xi\eta} \cdot \sum_j v_j^{\eta} | \xi; \eta_j). \end{aligned} \quad (C-25)$$

Because of the oddness of the undifferentiated part of $u_{ij}^{\xi\eta}$ this is zero.

After simplification, the final result for the cross term in the energy is

$$\begin{aligned} 2 \sum_{\xi} \sum_{\eta < \rho} \sum_{\rho} \Lambda^{\xi} (\lambda^{\eta\rho} + \lambda^{\rho\eta}) = \quad (C-26) \\ = 2 \sum_{\xi < \eta} (\lambda^{\xi\eta} + \lambda^{\eta\xi}) \left\{ (\xi; \eta_j | u_{ij}^{\xi\eta} v_{ij} (\Lambda^{\xi} v_i^{\xi} + \Lambda^{\eta} v_j^{\eta}) | \xi; \eta_j) \right. \\ \left. - (\xi; \eta_j | u_{ij}^{\xi\eta} v_{ij} | \xi; \eta_j) \cdot \right. \\ \left. \cdot [\Lambda^{\xi} (\xi | v^{\xi} | \xi) + \Lambda^{\eta} (\eta | v^{\eta} | \eta)] \right\} \\ - 2 \sum_{\xi < \eta} (\lambda^{\xi\eta} + \lambda^{\eta\xi}) (\xi; \eta_j | u_{ij}^{\xi\eta} v_{ij} | \xi; \eta_j) \sum_{\rho} \Lambda^{\rho} (\rho | v^{\rho} | \rho). \end{aligned}$$

At first this term appears somewhat strange. The first part is of the form "matrix element of the product less the product of matrix elements" which we have encountered before. The second part is of a new type.

The first term arises in the following way. If we had had foresight, we could have normalized the variational wave function to terms correct in the first power of λ by using as the additional term $\lambda^2 (\psi^2(x_i) - \langle \psi | \psi^2 | \psi \rangle) \phi^2$ rather than $\lambda^2 \psi^2(x_i) \phi^2$. This would have introduced just the first two lines of (C-26). The factor of 2 arises from the additional term in both the bra and the ket.

However, since we did not make this choice, the wave function is not normalized and the Van der Waals energy calculated from it will be too big by the amount the wave function exceeds its normalized value. We must therefore subtract from the energy the Van der Waals interaction times the excess. This is the second term in (C-26).

From (C-26) we have the Van der Waals correction to Λ^{ξ}

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

(C-27)

2. The Spin-Orbit Parameter $\mathcal{L}^{\xi}$

a. The spin-orbit energy

The contribution to the energy involving $\mathcal{L}$'s is

$$E_{\mathcal{L}} = \sum_{\xi} 2 i_{\xi} \mathcal{L}^{\xi} + \sum_{\xi} \sum_{\eta} j_{\xi\eta} \mathcal{L}^{\xi} \mathcal{L}^{\eta} \quad (\text{C-28})$$

$$+ \sum_{\xi} \sum_{\eta} 2 K_{\xi\eta} \Lambda^{\xi} \mathcal{L}^{\eta} + \sum_{\xi} \sum_{\eta} \sum_{\rho \neq \eta} 2 M_{\xi,\eta\rho} \mathcal{L}^{\xi} \mathcal{L}^{\eta\rho}$$

From Eq. (7-4) these terms are

$$\sum_{\xi} 2 i_{\xi} \mathcal{L}^{\xi} = \quad (\text{C-29a})$$

$$= \langle u_2 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_2 \rangle -$$

$$- \langle u_0 | \mathcal{H}' | u_0 \rangle [\langle u_2 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_2 \rangle]$$

$$\sum_{\xi} \sum_{\eta} j_{\xi\eta} \mathcal{L}^{\xi} \mathcal{L}^{\eta} = \quad (\text{C-29b})$$

$$= \langle u_2 | \mathcal{H}' | u_2 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_2 | \mathcal{H}' | u_2 \rangle$$

$$- 2 \langle u_2 | u_0 \rangle [\langle u_2 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_2 \rangle +$$

$$- 2 \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_2 | u_0 \rangle]$$

$$\sum_{\xi} \sum_{\eta} 2 K_{\xi,\eta} \Lambda^{\xi} \mathcal{L}^{\eta}$$

= Defined in Section 1
as Eq. (C-2c)

$$\begin{aligned}
\sum_{\xi} \sum_{\eta} \sum_{\rho \neq \eta} 2 M_{\xi, \eta \rho} \mathcal{L}^{\xi} \lambda^{\eta \rho} &= \\
&= \langle u_2 | \mathcal{H}' | u_3 \rangle + \langle u_3 | \mathcal{H}' | u_2 \rangle \\
&\quad - \langle u_0 | \mathcal{H}' | u_0 \rangle [\langle u_2 | u_3 \rangle + \langle u_3 | u_2 \rangle] \\
&\quad - 2 [2 \langle u_2 | u_0 \rangle \langle u_0 | \mathcal{H}' | u_3 \rangle + \\
&\quad + (\langle u_2 | \mathcal{H}' | u_0 \rangle + \langle u_0 | \mathcal{H}' | u_2 \rangle) \langle u_0 | u_3 \rangle \\
&\quad - 4 \langle u_2 | u_0 \rangle \langle u_0 | u_3 \rangle \langle u_0 | \mathcal{H}' | u_0 \rangle].
\end{aligned}
\tag{C-29c}$$

The $\mathcal{L}^{\xi}$ corresponding to minimum energy is

$$\begin{aligned}
\mathcal{L}^{\xi} &= - \frac{i_{\xi}}{j_{\xi\xi}} - \\
&\quad - \frac{\sum_{\eta \neq \xi} \frac{1}{2} (j_{\xi\eta} + j_{\eta\xi}) \mathcal{L}^{\eta} + \sum_{\eta} K_{\eta\xi} \Lambda^{\eta} + \sum_{\eta} \sum_{\rho} M_{\xi, \eta \rho} (\lambda^{\eta \rho} + \lambda^{\rho \eta})}{j_{\xi\xi}}.
\end{aligned}
\tag{C-30}$$

In Chapter VIII of the text it is shown that the spin-orbit parameter only appears in the formulas for the g-shift. It is further shown in Section 2.c of Appendix D that spin-orbit effects in the crystalline hydrogen wave function lead to no shift, the shift in g to first power in $\mathcal{L}^{\xi}$ arising solely from the argon spin-orbit interaction. Formula (8-8) for the g-shift shows that it is second order in the overlap to start with. It is therefore only necessary to calculate $\mathcal{L}^{\xi}$ to first order. We need never calculate $\mathcal{L}^{\circ}$ as far as

the g-shift is concerned since its effects are identically zero.

Clearly, however, $\mathcal{L}^0$ will arise only from the spin-orbit interaction of the argon p, σ states admixed into the hydrogen function by orthogonalization. $\mathcal{L}^0$ will therefore be the $\mathcal{L}^*$ associated with the admixed function. Furthermore, to find the wave function to order S^2 we need find $\mathcal{L}^0$ to order S^0 only since the only contribution of $\mathcal{L}^0 \omega^0 \mathcal{L}^0$ comes from its operation on the admixed function.

b. The $i \xi$ term

To calculate $i \xi$ we need not consider correlation effects. We therefore replace the $1/r_{ij}$ term in the Hamiltonian by the average crystal field and use as our Hamiltonian Eq. (C-20). We have shown that the matrix elements of $\sum' V_{\xi}(r_i)$ are of order S^2 and so we shall neglect them in calculating $i \xi$ to order S^0 . Particular care must be taken to keep all exchange terms since these are of order S^0 for intra-atomic exchange.

From Eq. (C-29a) and Appendix B we have to order S^0

$$\begin{aligned}
 \sum_{\xi} 2 i_{\xi} \mathcal{L}^{\xi} &= \quad (C-31) \\
 &= \sum_{\xi} \mathcal{L}^{\xi} \left\{ (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} (\mathcal{H}_0 + h_{s.o.}) | \xi) + (\xi | (\mathcal{H}_0 + h_{s.o.}) \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) \right. \\
 &\quad - \sum_{\eta} \left[(\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | \mathcal{H}_0 + h_{s.o.} | \xi) + \right. \\
 &\quad \left. \left. + (\xi | \mathcal{H}_0 + h_{s.o.} | \eta) (\eta | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) \right] \right\}.
 \end{aligned}$$

The energy eigenvalues cancel leaving just $h_{s.o.}$ terms.

Substituting $h_{s.o.} = \chi \underline{L} \cdot \underline{\sigma}$ and using the assumption that $\omega^{\xi}(\underline{r})$ is spherically symmetric, we have

$$\begin{aligned}
 i_{\xi} &= (\xi | \chi \omega^{\xi} (\underline{L} \cdot \underline{\sigma})^2 | \xi) - \quad (C-32) \\
 &\quad - \sum_{\eta} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | \chi \underline{L} \cdot \underline{\sigma} | \xi).
 \end{aligned}$$

Since we seek i_{ξ} to order S^0 , η runs over states centered on the same atom as φ^{ξ} .

Now, $\varphi^{\xi} = R^{\xi}(\underline{r}) Y^{\xi}(\theta, \varphi) \delta(\xi)$ where $R^{\xi}(\underline{r})$ is the radial part of φ^{ξ} , $Y^{\xi}(\theta, \varphi)$ is its angular dependence and $\delta(\xi)$ is its spin function. Then the expression for i_{ξ} may be separated into radial and angular-spin parts.

$$\begin{aligned}
i_{\xi} = & (R^{\xi} | \chi \omega^{\xi} | R^{\xi}) (Y^{\xi} \delta(\xi) | (\underline{L} \cdot \underline{\sigma})^2 | Y^{\xi} \delta(\xi)) - \\
& - \sum_{\eta} (R^{\xi} | \omega^{\xi} | R^{\eta}) (R^{\eta} | \chi | R^{\xi}) \cdot \\
& \cdot (Y^{\xi} \delta(\xi) | \underline{L} \cdot \underline{\sigma} | Y^{\xi} \delta(\xi))^2.
\end{aligned}$$

(C-33)

Within a given subshell the radial part will be the same for each electron. The second term may therefore be summed over the spin-angular terms within a given subshell. Within a subshell, the $Y_{\ell}^m \delta(\xi)$'s form a complete set for angular operators. So by completeness we have

$$\begin{aligned}
i_{\xi} = & \left\{ (R^{\xi} | \chi \omega^{\xi} | R^{\xi}) - \sum_{\substack{\eta, \text{ shells} \\ L \neq 0}} (R^{\xi} | \omega^{\xi} | R^{\eta}) (R^{\eta} | \chi | R^{\xi}) \right\} \cdot \\
& \cdot (Y^{\xi} \delta(\xi) | (\underline{L} \cdot \underline{\sigma})^2 | Y^{\xi} \delta(\xi)).
\end{aligned}$$

(C-34)

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

c. The $j_{\xi\eta}$ terms

We shall evaluate these terms in two parts as we did in the case of J. The two terms are

$$j_1 = \langle u_2 | \mathcal{H}' | u_2 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_2 | \mathcal{H}' | u_2 \rangle$$

$$j_2 = -2 \langle u_2 | u_0 \rangle [\langle u_2 | u' | u_0 \rangle + \langle u_0 | u' | u_2 \rangle - 2 \langle u_0 | u' | u_0 \rangle \langle u_2 | u_0 \rangle] \quad (C-35)$$

To evaluate these we shall use the same Hamiltonian as for i_ξ , viz., $\mathcal{H}'(u_i) = \mathcal{H}_0(u_i) + h_{so.}(u_i)$, where we have neglected the crystal field. On expanding and regrouping terms we have, in terms of the function $\xi_2 = \omega^\xi \underline{u} \cdot \underline{\sigma} \phi^\xi$

$$\begin{aligned} j_1 = & \sum_{\xi} \langle \xi_2 | \mathcal{H} | \xi_2 \rangle - \\ & - \sum_{\xi} \sum_{\eta} \langle \xi_2 | \eta_2 \rangle \langle \eta | \mathcal{H} | \xi \rangle \\ & + \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_2 | \eta_j | \mathcal{H}_i + \mathcal{H}_j | \xi_2 \eta_j \rangle - \langle \xi_2 | \eta_j | \mathcal{H}_i + \mathcal{H}_j | \eta_i \xi_2 \rangle \\ & - \sum_{\xi} \sum_{\eta \neq \xi} [\langle \xi_2 | \eta_j | \xi_i \eta_{2j} \rangle - \langle \xi_2 | \eta_j | \eta_i \xi_{2j} \rangle] \cdot \\ & \cdot [\langle \xi | \mathcal{H} | \xi \rangle + \langle \eta | \mathcal{H} | \eta \rangle] \\ & - \sum_{\xi} \sum_{\eta \neq \xi} \sum_{\rho \neq \xi, \eta} \left\{ [\langle \xi_2 | \eta_j | \xi_i \rho_j \rangle - \langle \xi_2 | \eta_j | \rho_i \xi_{2j} \rangle] \langle \rho | \mathcal{H} | \eta \rangle \right. \\ & \left. + [\langle \xi_2 | \eta_j | \rho_i \eta_{2j} \rangle - \langle \xi_2 | \eta_j | \eta_i \rho_{2j} \rangle] \langle \rho | \mathcal{H} | \xi \rangle \right\} \cdot \quad (C-36) \end{aligned}$$

Before continuing, consider the first term

$\langle \xi_2 | \mathcal{H}_0(u_i) | \xi_2 \rangle$. This may be reduced as was $\langle \xi | u^\xi \mathcal{H}_0 u^\xi | \xi \rangle$ by integration by parts. The result is

$$\frac{1}{2} (\xi | \nabla(\omega^\xi \underline{u} \cdot \underline{\sigma}) \cdot \nabla(\omega^\xi \underline{u} \cdot \underline{\sigma}) | \xi) + \epsilon_\xi (\xi | (\omega^\xi \underline{u} \cdot \underline{\sigma})(\omega^\xi \underline{u} \cdot \underline{\sigma}) | \xi).$$

Substituting $H_1 = H_{01} + h_{s0}$ and canceling the resulting energy eigenvalues we have

$$\begin{aligned}
 j_1 = & \sum_{\xi} \mathcal{L}^{\xi^2} \left\{ \frac{1}{2} (\xi | \nabla (\omega^{\xi} \underline{h} \cdot \underline{\sigma}) \cdot \nabla (\omega^{\xi} \underline{h} \cdot \underline{\sigma}) | \xi) + \right. \quad (C-37) \\
 & + (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} h_{s.o.} \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \xi) \\
 & - (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \xi) (\xi | h_{s.o.} | \xi) \} \\
 & - \sum_{\xi} \sum_{\eta \neq \xi} \mathcal{L}^{\xi} \mathcal{L}^{\eta} (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} \omega^{\eta} \underline{h} \cdot \underline{\sigma} | \eta) (\eta | h_{s.o.} | \xi) \\
 & + \sum_{\xi} \mathcal{L}^{\xi^2} \sum_{\eta \neq \eta} (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \eta) (\eta | \omega^{\eta} \underline{h} \cdot \underline{\sigma} | \xi) (E_{\xi} - E_{\eta}) \\
 & + \sum_{\xi} \sum_{\eta \neq \xi} \mathcal{L}^{\xi} \mathcal{L}^{\eta} (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \xi) \\
 & \cdot \{ (\eta | h_{s.o.} \omega^{\eta} \underline{h} \cdot \underline{\sigma} | \eta) - (\eta | \omega^{\eta} \underline{h} \cdot \underline{\sigma} | \eta) (\eta | h_{s.o.} | \eta) \} \\
 & + \mathcal{L}^{\xi} \mathcal{L}^{\eta} (\eta | \omega^{\eta} \underline{h} \cdot \underline{\sigma} | \eta) \\
 & \cdot \{ (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} h_{s.o.} | \xi) - (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \xi) (\xi | h_{s.o.} | \xi) \} \\
 & - \mathcal{L}^{\xi^2} (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \eta) \\
 & \cdot \{ (\eta | h_{s.o.} \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \xi) - (\eta | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \xi) (\eta | h_{s.o.} | \eta) \} \\
 & - \mathcal{L}^{\xi^2} (\eta | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \xi) \\
 & \cdot \{ (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} h_{s.o.} | \eta) - (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \eta) (\xi | h_{s.o.} | \eta) \} \\
 & - \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \xi} \mathcal{L}^{\xi} [\mathcal{L}^p (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \xi) (\eta | \omega^p \underline{h} \cdot \underline{\sigma} | p) - \\
 & - \mathcal{L}^{\xi} (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | p) (\eta | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \xi)] (p | h_{s.o.} | \eta) \\
 & - \sum_{\xi} \sum_{\eta \neq \xi} \sum_{p \neq \eta} \mathcal{L}^{\xi} [\mathcal{L}^{\eta} (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | p) (\eta | \omega^{\eta} \underline{h} \cdot \underline{\sigma} | \eta) - \\
 & - \mathcal{L}^p (\xi | \omega^{\xi} \underline{h} \cdot \underline{\sigma} | \eta) (\eta | \omega^p \underline{h} \cdot \underline{\sigma} | p)] (p | h_{s.o.} | \xi).
 \end{aligned}$$

From Eqs. (C-29b) and (C-32) we have for j_2

$$\begin{aligned}
 j_2 = & \\
 = & -2 \sum_{\xi} \sum_p \mathcal{L}^{\xi} \mathcal{L}^p \langle p | \omega^p \underline{L} \cdot \underline{\sigma} | p \rangle \cdot \\
 & \cdot \left\{ \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} h_{s.o.} | \xi \rangle + \langle \xi | h_{s.o.} \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi \rangle \right. \\
 & \left. - 2 \sum_{\eta} \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta \rangle \langle \eta | h_{s.o.} | \xi \rangle \right\} \quad (C-38)
 \end{aligned}$$

Now consider $\nabla \omega^{\xi} \underline{L} \cdot \underline{\sigma}$, for the case of ω^{ξ} , a function of distance from the nucleus on which φ^{ξ} is centered, i.e., s-like. First,

$$\begin{aligned}
 \nabla (\underline{L} \cdot \underline{\sigma}) &= \nabla (\underline{r} \times \underline{p} \cdot \underline{\sigma}) = \nabla (\underline{r} \cdot \underline{p} \times \underline{\sigma}) \\
 &= \left[\frac{\partial}{\partial r} \underline{r} \cdot \underline{p} \times \underline{\sigma} \right] \hat{r} \\
 &= \frac{1}{r} \underline{L} \cdot \underline{\sigma} \hat{r}.
 \end{aligned}$$

So for $\omega^{\xi}(\underline{r}) = \omega^{\xi}(|\underline{r} - \underline{R}|)$,

$$\nabla \omega^{\xi}(\underline{L} \cdot \underline{\sigma}) = \left[\frac{\partial \omega^{\xi}(\underline{r})}{\partial r} + \frac{\omega^{\xi}(\underline{r})}{r} \right] \underline{L} \cdot \underline{\sigma} \hat{r}. \quad (C-39)$$

$j_{\xi\xi}$ consists of two types of terms, those derived from the operators involving ∇ and those involving the spin-orbit operator. Representative matrix elements for these terms are

$$(\xi | (\frac{\partial \omega^{\frac{1}{2}}}{\partial r} + \frac{\omega^{\frac{1}{2}}}{r})^2 (\frac{L \cdot S}{2}) | \xi) \quad (C-40a)$$

and

$$(\xi | \chi \omega^{\frac{1}{2}} (\frac{L \cdot S}{2}) | \xi) \quad (C-40b)$$

respectively. Now, $\chi = \frac{\hbar^2}{4m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r}$ and near the nucleus of an argon atom $V \sim 18/r$ so that near the nucleus χ in atomic units is $\chi \sim 2.4 \times 10^{-4} r^{-3}$.

A trial calculation was made for the argon 3p state in which all terms in $j \xi \xi$ that involved χ were neglected and $\omega^{\frac{1}{2}}$ was taken as $r^{n'}$. It was found that minimum energy occurred for $n' = 0.9$. So, to estimate the importance of the terms involving the spin-orbit term let us take $\omega^{\frac{1}{2}} = r$ or $n' = 1$. Then, $(\frac{\partial \omega^{\frac{1}{2}}}{\partial r} + \frac{\omega^{\frac{1}{2}}}{r})^2 = 4$ and $\chi \omega^{\frac{1}{2}} = 2.4 \times 10^{-4} \times r^{-2}$.

Using these values, the radial integral for (C-40a) will be 4 for normalized radial functions. The main contribution to (C-40b) will come from very near the nucleus, the operator in (C-40b) equaling that of (C-40a) only for $r \approx 6 \times 10^{-3} a_0$. From 0 to 0.01 the argon 3p radial function is approximately 50 r. At 0.3 a_0 this overestimates the function by a factor of over twenty. The contribution of the interval from ∞ to 0.3 a_0 to the radial part of term (C-40b) cannot exceed 2.7×10^{-3} and, using the asymptotic wave func-

tions, the interval from 0.3 to 0 contributes less than

$$(50)^2 \times 2.4 \times 10^{-4} \cdot \int_0^{0.3} r^2 dr = 1.3 \times 10^{-3}. \text{ On the}$$

strength of this estimate we can conclude that it is consistent to neglect spin-orbit terms in calculating

$$j_{\xi\xi}.$$

$j_{\xi\xi}$ can be further simplified by separating the radial and angular matrix elements and then summing over the closed shells of the argon atoms, keeping in mind that the radial integrals are the same within each shell. The final form is

$$j_{\xi\xi} = \left\{ \frac{1}{2} (R^{\xi} | \left(\frac{\partial \omega^{\xi}}{\partial r} + \frac{\omega^{\xi}}{r} \right)^2 | R^{\xi}) \right. \\ \left. - \sum_{\substack{\eta \text{ shells} \\ \omega + \eta = L+0}} (R^{\xi} | \omega^{\xi}(r) | R^{\eta})^2 (E_{\eta} - E_{\xi}) \right\} \cdot \\ \cdot (Y^{\xi}_{\delta(\xi)} | (\underline{L} \cdot \underline{\sigma})^2 | Y^{\xi}_{\delta(\xi)}).$$

(C-41)

The $j_{\xi\eta} \quad \eta \neq \xi$ terms arise from the spin-orbit term in the Hamiltonian. As a representative term let us consider

$$(\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) (\eta | \omega^{\eta} \underline{L} \cdot \underline{\sigma} | \eta). \quad (C-42)$$

This appears in the formula for L^{ξ} multiplied by L^{η} and divided by $j_{\xi\xi}$. From our estimates of the matrix elements involving $\mathcal{K}$, this must represent a correction to L^{ξ} of some three orders of magnitude less than the $i_{\xi}/j_{\xi\xi}$ term. We shall therefore neglect any $j_{\xi\eta}, \eta \neq \xi$ terms.

d. The $K_{\xi\eta}$ terms

These terms were evaluated in the preceding section and are given by Eq. (C-21). In our approximation, the sum over η in $\sum_{\eta} K_{\eta,\xi} \Lambda^{\eta}$ has only one term for φ^{η} , the hydrogen 1s state. This is zero to order S^0 because of the combination $\underline{L} \cdot \underline{\sigma}$ operating on the 1s function. More generally this term will not contribute in molecular crystals since we seek the cross terms to order S^0 while Λ is of order S^2 to start with.

e. The $M_{\xi,\eta\rho}$ term

This term is similar to $L_{\xi,\eta\rho}$ evaluated in Section 1.c of this Appendix. Because of the oddness of $u_{ij}^{\xi\eta}$ the only cross terms that are non-zero are

$$\begin{aligned} \sum_{\xi} \sum_{\eta < \rho} 2 M_{\xi,\eta\rho} L^{\xi} (\lambda^{\eta\rho} + \lambda^{\rho\eta}) &= \\ &= \langle u_2 | \mathcal{K}' | u_3 \rangle + \langle u_3 | \mathcal{K}' | u_2 \rangle \\ &\quad - 4 \langle u_2 | u_0 \rangle \langle u_3 | \mathcal{K}' | u_0 \rangle. \end{aligned} \tag{C-43}$$

As in Section 1.e we shall use the approximate Hamiltonian given by Eq. (C-22) in which the interaction of electrons on one atom with the rest of the crystal is given by the dipole-dipole term of the multipole expansion. Inclusion of the spin-orbit term would lead to nothing new since ω^3 is spherically symmetric and would integrate to zero when combined with $u_{ij}^{\xi\eta}$. The result may be written down in analogy with Eq. (C-27) for

$\sum_{\xi} \sum_{\rho} L_{\xi, \eta \rho} (\lambda^{\eta \rho} + \lambda^{\rho \eta})$. The resulting contribution to $\mathcal{L}^{\xi}$

is

$$\begin{aligned} \sum_{\eta < \rho} M_{\xi, \eta \rho} (\lambda^{\eta \rho} + \lambda^{\rho \eta}) &= \quad (C-44) \\ &= (\lambda^{\xi 0} + \lambda^{0 \xi}) \left\{ (o_i \xi_j | u_{ij}^{0 \xi} v_{ij} | \omega^3(x_j) L_j \cdot \sigma | o_i \xi_j) \right. \\ &\quad \left. - (o_i \xi_j | u_{ij}^{0 \xi} v_{ij} | o_i \xi_j) (\xi | \omega^3 L \cdot \sigma | \xi) \right\} \\ &\quad - \sum_{\rho < \xi} (\lambda^{\rho 0} + \lambda^{0 \rho}) (o_i \rho_j | u_{ij}^{0 \rho} v_{ij} | o_i \rho_j) (\xi | \omega^3 L \cdot \sigma | \xi) \end{aligned}$$

In deriving this we have used the assumption that we only consider the Van der Waals interaction between hydrogen and argon. Thus only $\lambda^{\rho 0}$ and $\lambda^{0 \rho}$ terms enter.

3. The Van der Waals Parameters, λ 's

a. The Van der Waals energy

The contribution to the energy involving the

λ 's is

$$\begin{aligned}
 E_{\lambda} = & \sum_{\xi} \sum_{\eta \neq \xi} 2 \pi_{\xi \eta} \lambda^{\xi \eta} + \sum_{\xi} \sum_{\eta \neq \xi} \sum_{\rho \neq \eta} \sum_{\nu \neq \rho} \gamma_{\xi \eta, \rho \nu} \lambda^{\xi \eta} \lambda^{\rho \nu} \\
 & + \sum_{\xi} \sum_{\eta} \sum_{\rho \neq \eta} 2 L_{\xi, \eta \rho} \lambda^{\xi} \lambda^{\eta \rho} \\
 & + \sum_{\xi} \sum_{\eta} \sum_{\rho \neq \eta} 2 M_{\xi, \eta \rho} \lambda^{\xi} \lambda^{\eta \rho}.
 \end{aligned}$$

(C-45)

From Eq. (7-4) these terms are

$$\sum_{\xi} \sum_{\eta \neq \xi} 2 \pi_{\xi \eta} \lambda^{\xi \eta} = \quad (C-46a)$$

$$= 2 [\langle u_3 | x' | u_0 \rangle - \langle u_0 | x' | u_0 \rangle \langle u_3 | u_0 \rangle]$$

$$\sum_{\xi} \sum_{\eta \neq \xi} \sum_{\rho} \sum_{\nu \neq \rho} \gamma_{\xi \eta, \rho \nu} \lambda^{\xi \eta} \lambda^{\rho \nu} = \quad (C-46b)$$

$$= \langle u_3 | x' | u_3 \rangle - \langle u_0 | x' | u_0 \rangle \langle u_3 | u_3 \rangle$$

$$- 4 \langle u_3 | u_0 \rangle [\langle u_3 | x' | u_0 \rangle -$$

$$- \langle u_0 | x' | u_0 \rangle \langle u_3 | u_0 \rangle].$$

The $L_{\xi, \eta \rho}$ and $M_{\xi, \eta \rho}$ terms are given by Eqs. (C-2d) and (C-29c) respectively.

Eqs. (C-46a and b) may be expanded as explained in Appendix A. However, it will be noticed that except for a factor of $\mathcal{B}_{ij}^{\xi\eta} = \lambda^{\xi\eta} u_{ij}^{\xi\eta}$ the expansions of (C-46a) and the first bracket of (C-46b) have the same form. We shall therefore give only the expansion of (C-46a).

Furthermore we note that in the expansion of (C-46b) terms like

$$\sum_{\xi} \sum_{\eta \neq \xi} \langle \xi i \eta j | \mathcal{B}_{ij}^{\xi\eta} (\text{operator}) \mathcal{B}_{ij}^{\xi\eta} | \xi i \eta j \rangle + \\ + \langle \xi i \eta j | \mathcal{B}_{ij}^{\xi\eta} (\text{operator}) \mathcal{B}_{ij}^{\eta\xi} | \xi i \eta j \rangle$$

will arise. From our choice of $u_{ij}^{\xi\eta} = u_{ji}^{\eta\xi}$ the matrix elements of $u_{ij}^{\xi\eta}$ in these are identical and the sum becomes

$$\sum_{\xi} \sum_{\eta \neq \xi} (\lambda^{\xi\eta} \lambda^{\xi\eta} + \lambda^{\xi\eta} \lambda^{\eta\xi}) \cdot (\xi i \eta j | u_{ij}^{\xi\eta} (\text{operator}) u_{ij}^{\xi\eta} | \xi i \eta j)$$

Here we see that $\lambda^{\xi\eta}$ and $\lambda^{\eta\xi}$ are strongly dependent on one another. That is, the assumption that the λ 's are only slightly coupled is not true, since $\chi_{\xi\eta, \xi\eta} = \chi_{\xi\eta, \eta\xi}$ and the iterative method of solution for $\lambda^{\xi\eta}$ breaks down.

However, by rewriting the summation the above

becomes

$$\sum_{\xi} \sum_{\eta} (\lambda^{\xi\eta} + \lambda^{\eta\xi})^2.$$

$$(\xi; \eta_j | \mathcal{U}_{ij}^{\xi\eta} (\text{Operator}) \mathcal{U}_{ij}^{\xi\eta} | \xi; \eta_j)$$

We can now use the iterative method to solve for $(\lambda^{\xi\eta} + \lambda^{\eta\xi})$. This is, of course, physically reasonable since we are calculating the Van der Waals interaction between two atoms and the effect cannot be divided between the atoms independently, but is a property of the system. Hence in our case, the sum of the Van der Waals parameter $\lambda^{\xi\eta}$ and $\lambda^{\eta\xi}$ has meaning, but separated, the individual terms do not.

The solution for the variational parameters now becomes

$$(\lambda^{\xi\eta} + \lambda^{\eta\xi}) = \tag{C-47}$$

$$= - \frac{\pi_{\xi\eta} + \sum_{\rho} \sum_{\nu} \frac{1}{2} (Y_{\xi\eta, \rho\nu} + Y_{\rho\nu, \xi\eta}) (\lambda^{\rho\nu} + \lambda^{\nu\rho})}{Y_{\xi\eta, \xi\eta}}$$

$$- \frac{\sum_{\rho} L_{\rho, \xi\eta} \Lambda^{\rho} + \sum_{\rho} M_{\rho, \xi\eta} \mathcal{L}^{\rho}}{Y_{\xi\eta, \xi\eta}}$$

b. The $\pi_{\xi\eta}$ term

Eq. (C-46a) when expanded yields

$$\langle u_3 | \mathcal{H}' | u_0 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_3 | u_0 \rangle = \quad (C-48)$$

$$= \sum_{\xi} \sum_{\eta \neq \xi} \lambda^{\xi\eta} \left\{ \langle \xi, \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi, \eta_j \rangle - \langle \xi, \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \eta_i, \xi_j \rangle \right.$$

$$- \left[\langle \xi, \eta_j, \eta_k | \frac{u_{ik}^{\xi\eta}}{r_{ik}} | \xi, \eta_j, \eta_k \rangle - \langle \xi, \eta_j, \eta_k | \frac{u_{ik}^{\xi\eta}}{r_{ik}} | \eta_i, \eta_j, \xi_k \rangle \right.$$

$$+ \langle \xi, \eta_j, \xi_k | \frac{u_{jk}^{\xi\eta}}{r_{jk}} | \xi, \eta_j, \xi_k \rangle - \langle \xi, \eta_j, \xi_k | \frac{u_{jk}^{\xi\eta}}{r_{jk}} | \xi_i, \xi_j, \eta_k \rangle$$

$$- \left(\langle \xi, \eta_j, \xi_k | \frac{u_{ik}^{\xi\eta}}{r_{ik}} | \eta_i, \xi_j, \xi_k \rangle - \langle \xi, \eta_j, \xi_k | \frac{u_{ik}^{\xi\eta}}{r_{ik}} | \xi_i, \xi_j, \eta_k \rangle \right.$$

$$\left. + \langle \xi, \eta_j, \eta_k | \frac{u_{ij}^{\xi\eta}}{r_{jk}} | \eta_i, \xi_j, \eta_k \rangle - \langle \xi, \eta_j, \eta_k | \frac{u_{ij}^{\xi\eta}}{r_{jk}} | \eta_i, \eta_j, \xi_k \rangle \right]$$

$$+ \left[\langle \xi, \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi, \eta_j \rangle - \langle \xi, \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \eta_i, \xi_j \rangle \right] \cdot$$

$$\cdot \left[\langle \xi, \eta_j | \frac{1}{r_{ij}} | \xi, \eta_j \rangle - \langle \xi, \eta_j | \frac{1}{r_{ij}} | \eta_i, \xi_j \rangle \right]$$

$$+ \left[\langle \xi, \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \rho, \eta_j \rangle - \langle \xi, \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \eta_i, \rho_j \rangle \right] \cdot$$

$$\cdot \left[\langle \rho, \eta_j | \frac{1}{r_{ij}} | \xi, \eta_j \rangle - \langle \rho, \eta_j | \frac{1}{r_{ij}} | \eta_i, \xi_j \rangle \right]$$

$$+ \left[\langle \xi, \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi, \rho_j \rangle - \langle \xi, \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \rho_i, \xi_j \rangle \right] \cdot$$

$$\cdot \left[\langle \rho, \xi_j | \frac{1}{r_{ij}} | \eta_i, \xi_j \rangle - \langle \rho, \xi_j | \frac{1}{r_{ij}} | \xi_i, \eta_j \rangle \right]$$

$$+ \sum_{\substack{\nu \neq \xi \\ \neq \eta \\ \neq \rho}} \langle \xi, \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \rho_i, \nu_j \rangle \cdot$$

$$\left[\langle \rho_i, \nu_j | \frac{1}{r_{ij}} | \xi_i, \eta_j \rangle - \langle \rho_i, \nu_j | \frac{1}{r_{ij}} | \eta_i, \xi_j \rangle \right] \Big\}$$

$$\begin{aligned}
& + \left\{ \sum_{\xi} \sum_{\eta \neq \xi} \langle \xi_i \eta_j | u_{ij}^{\xi \eta} (H_i + H_j) | \xi_i \eta_j \rangle + \right. \\
& \quad + \sum_{p \neq \xi} \langle \xi_i \eta_j p_k | \frac{u_{ij}^{\xi \eta}}{r_{ik}} | \xi_i \eta_j p_k \rangle - \langle \xi_i \eta_j p_k | \frac{u_{ij}^{\xi \eta}}{r_{ik}} | p_i \eta_j \xi_k \rangle \\
& \quad + \sum_{p \neq \eta} \langle \xi_i \eta_j p_k | \frac{u_{ij}^{\xi \eta}}{r_{jk}} | \xi_i \eta_j p_k \rangle - \langle \xi_i \eta_j p_k | \frac{u_{ij}^{\xi \eta}}{r_{jk}} | \xi_i p_j \eta_k \rangle \\
& \quad - \left[\langle \xi_i \eta_j | u_{ij}^{\xi \eta} (H_i + H_j) | \eta_i \xi_j \rangle + \right. \\
& \quad + \sum_{p \neq \xi} \langle \xi_i \eta_j p_k | \frac{u_{ij}^{\xi \eta}}{r_{ik}} | \eta_i \xi_j p_k \rangle - \langle \xi_i \eta_j p_k | \frac{u_{ij}^{\xi \eta}}{r_{ik}} | p_i \xi_j \eta_k \rangle + \\
& \quad + \sum_{p \neq \xi} \langle \xi_i \eta_j p_k | \frac{u_{ij}^{\xi \eta}}{r_{jk}} | \eta_i \xi_j p_k \rangle - \langle \xi_i \eta_j p_k | \frac{u_{ij}^{\xi \eta}}{r_{jk}} | \eta_i p_j \xi_k \rangle \Big] \\
& \quad - \left[\langle \xi_i \eta_j | H_i + H_j | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | H_i + H_j | \eta_i \xi_j \rangle + \right. \\
& \quad + \sum_{v \neq \xi} \langle \xi_i \eta_j | \frac{1}{r_{ij}} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | \frac{1}{r_{ij}} | v_i \xi_j \rangle \\
& \quad + \sum_{v \neq \eta} \langle \eta_i \eta_j | \frac{1}{r_{ij}} | \eta_i \eta_j \rangle - \langle \eta_i \eta_j | \frac{1}{r_{ij}} | v_i \eta_j \rangle \Big] \cdot \\
& \quad \cdot \left[\langle \xi_i \eta_j | u_{ij}^{\xi \eta} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | u_{ij}^{\xi \eta} | \eta_i \xi_j \rangle \right] \Big\} \\
& - \left\{ \sum_{\substack{p \neq \xi \\ p \neq \eta}} \left[\langle \xi_i \eta_j | u_{ij}^{\xi \eta} | p_i \eta_j \rangle - \langle \xi_i \eta_j | u_{ij}^{\xi \eta} | \eta_i p_j \rangle \right] \cdot \right. \\
& \quad \cdot \left[\langle p | H | \xi \rangle + \sum_{v \neq \xi} \langle p_i \eta_j | \frac{1}{r_{ij}} | \xi_i \eta_j \rangle - \langle p_i \eta_j | \frac{1}{r_{ij}} | v_i \xi_j \rangle \right] \\
& \quad \left[\langle \xi_i \eta_j | u_{ij}^{\xi \eta} | \xi_i p_j \rangle - \langle \xi_i \eta_j | u_{ij}^{\xi \eta} | p_i \xi_j \rangle \right] \cdot \\
& \quad \cdot \left[\langle p | H | \eta \rangle + \sum_{v \neq \eta} \langle p_i \eta_j | \frac{1}{r_{ij}} | \eta_i \eta_j \rangle - \langle p_i \eta_j | \frac{1}{r_{ij}} | v_i \eta_j \rangle \right] \Big\}.
\end{aligned}$$

This expansion has been divided into three parts. The first and most important term is the electrostatic interaction between the corrected electronic states ϕ^ξ and ϕ^η . This and exchange corrections are included in the first set of braces. The second term enclosed in braces is the "atomic" energies of states ϕ^ξ and ϕ^η modified for the charges in the wave functions ϕ^ξ and ϕ^η . The third term is an exchange correction to the second term.

The expansion in atomic function of Eq. (C-48) is extremely complicated if all terms of order S^2 are included. Much of the complication comes from matrix elements like $\langle \xi_i \eta_j | \frac{1}{r_{ik}} | \xi_i \eta_j \rangle$ etc. in the second and third terms. Since they represent exchange corrections to potentials we shall approximate them by the exchange-corrected atomic potential $\tilde{\Sigma}' V$ defined in Eq. (7-18). Then the second brace becomes

$$\begin{aligned}
 & \langle \xi_i \eta_j | u_{ij}^{\xi\eta} (H_{0i} + \tilde{\Sigma}' V_\xi(x_i) | \xi_i \eta_j \rangle - \longleftrightarrow \\
 & + \langle \xi_i \eta_j | u_{ij}^{\xi\eta} (H_{0j} + \tilde{\Sigma}' V_\eta(x_j) | \xi_i \eta_j \rangle - \longleftrightarrow \\
 & - [\langle \xi | H_0 + \tilde{\Sigma}' V_\xi(x_i) | \xi \rangle \\
 & \quad + \langle \eta | H_0 + \tilde{\Sigma}' V_\eta(x_j) | \eta \rangle] \cdot \\
 & \cdot [\langle \xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | u_{ij}^{\xi\eta} | \eta_i \xi_j \rangle]
 \end{aligned} \tag{C-49}$$

A similar expansion may be made for the third brace.

The results of expanding the second and third braces after assuming an exchange potential are given in Eqs. (C-50) and (C-51) respectively.

The second brace of (C-48)

$$\begin{aligned}
 & [(\xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \eta_j) - (\xi_i \eta_i | u_{ij}^{\xi\eta} | \eta_i \xi_j)] \cdot \\
 & \cdot [1 - S_{\alpha\xi}^2 (\frac{1}{4} \epsilon_\alpha + \frac{1}{4} \epsilon_\xi - \frac{1}{2} \epsilon_\eta) \\
 & - S_{\alpha\eta}^2 (\frac{1}{4} \epsilon_\alpha + \frac{1}{4} \epsilon_\eta - \frac{1}{2} \epsilon_\xi)] \\
 & + (\xi_i \eta_j | u_{ij}^{\xi\eta} (\tilde{\Sigma}' V_\xi(x_i) + \tilde{\Sigma}' V_\eta(x_j)) | \xi_i \eta_j) \\
 & - (\xi_i \eta_j | u_{ij}^{\xi\eta} (\tilde{\Sigma}' V_\eta(x_i) + \tilde{\Sigma}' V_\xi(x_j)) | \eta_i \xi_j) \\
 & - [(\xi | \tilde{\Sigma}' V_\xi | \xi) + (\eta | \tilde{\Sigma}' V_\eta | \eta)] \cdot \\
 & [(\xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \eta_j) - (\xi_i \eta_j | u_{ij}^{\xi\eta} | \eta_i \xi_j)] \\
 & - \frac{1}{2} \sum_{\alpha \neq \xi} S_{\alpha\xi} \left\{ [(\xi_i \eta_j | u_{ij}^{\xi\eta} | \alpha_i \eta_j) - \leftrightarrow] (\epsilon_\alpha - \epsilon_\xi) \right. \\
 & + (\alpha_i \eta_j | u_{ij}^{\xi\eta} [\tilde{\Sigma}' V_\xi(x_i) + \tilde{\Sigma}' V_\eta(x_j)] | \xi_i \eta_j) - \leftrightarrow \\
 & + (\xi_i \eta_j | u_{ij}^{\xi\eta} [\tilde{\Sigma}' V_\alpha(x_i) + \tilde{\Sigma}' V_\alpha(x_j)] | \alpha_i \eta_j) - \leftrightarrow \\
 & + [(\alpha_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \eta_j) - (\alpha_i \eta_j | u_{ij}^{\xi\eta} | \eta_i \xi_j) \\
 & + (\xi_i \eta_j | u_{ij}^{\xi\eta} | \alpha_i \eta_j) - (\xi_i \eta_j | u_{ij}^{\xi\eta} | \eta_i \alpha_j)] \cdot \\
 & \cdot [(\xi | \tilde{\Sigma}' V_\xi | \xi) + (\eta | \tilde{\Sigma}' V_\eta | \eta)] \\
 & \hspace{15em} (C-50)
 \end{aligned}$$

$$- [(\xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \eta_j) - (\xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \eta_j)] \cdot$$
$$\cdot [(\alpha | \tilde{Z}' V_\xi | \xi) - (\xi | \tilde{Z}' V_\alpha | \alpha)] \}$$
$$-\frac{1}{2} \sum_{\alpha \neq \eta} S_{\alpha\eta} \left\{ [(\xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \alpha_j) - \longleftrightarrow] (\epsilon_\alpha - \epsilon_\eta) \right.$$
$$+ (\xi_i \alpha_j | u_{ij}^{\xi\eta} [\tilde{Z}' V_\xi(x_i) + \tilde{Z}' V_\eta(x_j)] | \xi_i \eta_j) - \longleftrightarrow$$
$$+ (\xi_i \eta_j | u_{ij}^{\xi\eta} [\tilde{Z}' V_\xi(x_i) + \tilde{Z}' V_\alpha(x_j)] | \xi_i \alpha_j) - \longleftrightarrow$$
$$- [(\xi_i \alpha_j | u_{ij}^{\xi\eta} | \xi_i \eta_j) - \longleftrightarrow$$
$$+ (\xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \alpha_j) - \longleftrightarrow]$$
$$\cdot [(\xi | \tilde{Z}' V_\xi | \xi) + (\eta | \tilde{Z}' V_\eta | \eta)]$$
$$- [(\xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \eta_j) - \longleftrightarrow]$$
$$\cdot [(\alpha | \tilde{Z}' V_\eta | \eta) + (\eta | \tilde{Z}' V_\alpha | \alpha)] \}$$
$$+\frac{3}{8} \sum_{\alpha \neq \beta} S_{\alpha\beta} S_{\beta\xi} (\xi_i \eta_j | u_{ij}^{\xi\eta} | \alpha_i \eta_j) (\epsilon_\alpha - \epsilon_\xi)$$
$$+\frac{3}{8} \sum_{\alpha \neq \eta} S_{\alpha\beta} S_{\beta\eta} (\xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \alpha_j) (\epsilon_\alpha - \epsilon_\eta)$$
$$+\frac{1}{4} \sum_{\alpha} S_{\alpha\xi} S_{\beta\eta} (\xi_i \eta_j | u_{ij}^{\xi\eta} | \beta_i \alpha_j) (\epsilon_\xi - \epsilon_\alpha)$$

The third brace of (C-48)

$$\begin{aligned} & [(\xi_i \eta_j | u_{ij}^{\xi \eta} | \rho_i \eta_j) - (\xi_i \eta_j | u_{ij}^{\xi \eta} | \eta_i \rho_j) \\ & - \frac{1}{2} S_{\rho} (\xi_i \eta_j | u_{ij}^{\xi \eta} | \alpha_i \eta_j) + \frac{1}{2} S_{\alpha \eta} (\xi_i \eta_j | u_{ij}^{\xi \eta} | \alpha_i \rho_j)] \cdot \\ & \cdot [S_{\rho \xi} (E_{\xi} + (\rho | \tilde{\Sigma}' V_{\xi} | \xi)) \\ & - \frac{1}{2} S_{\rho \alpha} E_{\alpha} - \frac{1}{2} S_{\rho \xi} E_{\rho}] \\ & + (\xi_i \eta_j | u_{ij}^{\xi \eta} | \xi_i \rho_j) [S_{\rho \eta} (E_{\eta} + (\rho | \tilde{\Sigma}' V_{\eta} | \eta))] \end{aligned}$$

(C-51)

An expansion in atomic functions of the first part of the term within the first brace of Eq. (C-48) is given in Eq. (C-52).

$$\begin{aligned}
 & \langle \xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \eta_i \xi_j \rangle = \\
 & = \left[(\xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi_i \eta_j) - (\xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \eta_i \xi_j) \right] \\
 & \quad \left(1 + \frac{3}{4} \sum_{\alpha} S_{\alpha\xi}^2 + \frac{3}{4} \sum_{\alpha} S_{\alpha\eta}^2 \right) \\
 & - \sum_{\alpha \neq \xi} \frac{1}{2} S_{\alpha\xi} \left[(\alpha_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi_i \eta_j) - (\alpha_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \eta_i \xi_j) \right. \\
 & \quad \left. + (\xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \alpha_i \eta_j) - (\xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \eta_i \alpha_j) \right] \\
 & - \sum_{\alpha \neq \eta} \left(\frac{1}{2} S_{\alpha\eta} - \frac{3}{8} \sum_{\beta} S_{\alpha\beta} S_{\beta\eta} \right) \\
 & \quad \left[(\xi_i \alpha_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi_i \eta_j) - (\xi_i \alpha_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \eta_i \xi_j) \right. \\
 & \quad \left. + (\xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi_i \alpha_j) - (\xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \alpha_i \xi_j) \right] \\
 & - \frac{1}{4} S_{\alpha\xi} S_{\beta\eta} (\xi_i \eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \beta_i \alpha_j) .
 \end{aligned}$$

(C-52)

The remaining terms within the first brace may be expanded according to Appendix B, but will not be given here because of their length. In making these expansions it should be noted that $u_{ij}^{\xi\eta}$ is a function with the part depending on $\underline{r}_i$ centered on the same center as φ^{ξ} and the part depending on $\underline{r}_j$ centered on the

same site as φ^{η} . This eliminates some terms since overlap terms are introduced in matrix elements if the wave functions are not on the same centers as $u_{i j}^{\xi \eta}$.

Since we have chosen $u_{i j}^{\xi \eta}$ as an odd function of coordinates $(\underline{r}_i - \underline{R}_I)$ and $(\underline{r}_j - \underline{R}_J)$ the direct terms of both the second and third parts of Eq. (C-48) are zero. Hence these represent exchange or S^2 corrections. On the other hand, the first part which includes terms involving $\frac{u_{i j}^{\xi \eta}}{r_{ij}}$ gives a contribution independent of overlap.

c. The $\Upsilon_{\xi \eta, p \nu}$ term

The $\Upsilon_{\xi \eta, p \nu}$ term will be evaluated in two parts, namely,

$$\begin{aligned} \Upsilon_1 &= \langle u_3 | \mathcal{H}' | u_3 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_3 | u_3 \rangle \\ \Upsilon_2 &= -4 \langle u_3 | u_0 \rangle \left[\langle u_3 | \mathcal{H}' | u_0 \rangle - \langle u_0 | \mathcal{H}' | u_0 \rangle \langle u_3 | u_0 \rangle \right] \end{aligned} \quad (C-53)$$

The first part, Υ_1 , has the same form as the $\Pi_{\xi \eta, p \nu}$ term with the exception of an extra $u_{i j}^{\xi \eta}$ in the ket. Hence, Υ_1 may be written down from (C-48) by adding a $u_{i j}^{\xi \eta}$ to the ket. However, in this case, the important terms in Υ_1 are those involving the Hamiltonian operating on the Van der Waals correction, such as

$\langle \xi_i \eta_j | u_{ij}^{\xi \eta} (H_{0i} + H_{0j}) u_{ij}^{\xi \eta} | \xi_i \eta_j \rangle$. In these terms the ∇^2 in the Hamiltonian differentiates the $u_{ij}^{\xi \eta}$ terms and gives a measure of the kinetic energy added by the correction. These terms will give rise to an S^0 contribution.

The second part, Υ_2 , is just $\langle u_3 | u_0 \rangle$ times the $\Pi_{\xi \eta}$ term already calculated. For the hydrogen-argon system the $\langle u_3 | u_0 \rangle$ term is just

$$\begin{aligned}
 \langle u_3 | u_0 \rangle &= \\
 &= \sum_0 \sum_{\langle \eta} (\lambda^{0\eta} + \lambda^{\eta 0}) [\langle \sigma_i \eta_j | u_{ij}^{0\eta} | \sigma_i \eta_j \rangle - \langle \sigma_i \eta_j | u_{ij}^{0\eta} | \eta_i \sigma_j \rangle] \\
 &= \sum_0 \sum_{\langle \eta} (\lambda^{0\eta} + \lambda^{\eta 0}) \cdot \\
 &\quad \cdot \{ [(\sigma_i \eta_j | u_{ij}^{0\eta} | \sigma_i \eta_j) - (\sigma_i \eta_j | u_{ij}^{0\eta} | \eta_i \sigma_j)] \\
 &\quad \cdot (1 + \frac{3}{4} \sum_{\alpha} S_{\alpha 0}^2 + \frac{3}{4} S_{0\eta}^2) \\
 &\quad - \frac{\sum_{\alpha \neq 0}}{2} S_{\alpha 0} [(\alpha \eta_j | u_{ij}^{0\eta} | \sigma_i \eta_j) - (\alpha \eta_j | u_{ij}^{0\eta} | \eta_i \sigma_j) \\
 &\quad + (\sigma_i \eta_j | u_{ij}^{0\eta} | \alpha \eta_j) - (\sigma_i \eta_j | u_{ij}^{0\eta} | \eta_i \alpha_j)] \\
 &\quad - \sum_{\alpha \neq \eta} (\frac{1}{2} S_{\alpha \eta} - \frac{3}{8} S_{\alpha 0} S_{0\eta}) \cdot \\
 &\quad [(\sigma_i \alpha_j | u_{ij}^{0\eta} | \sigma_i \eta_j) - (\sigma_i \alpha_j | u_{ij}^{0\eta} | \eta_i \sigma_j) \\
 &\quad + (\sigma_i \eta_j | u_{ij}^{0\eta} | \sigma_i \alpha_j) - (\sigma_i \eta_j | u_{ij}^{0\eta} | \alpha_i \sigma_j)] \\
 &\quad - \sum_{\alpha} \sum_{\beta} \frac{1}{4} S_{\alpha 0} S_{0\eta} (\sigma_i \eta_j | u_{ij}^{0\eta} | \sigma_i \alpha_j) \cdot \quad (C-54)
 \end{aligned}$$

This is zero to order S^2 since $u_{ij}^{\xi\eta}$ is odd. χ_2 therefore will contribute only a small S^2 correction to $\chi_{\xi\eta,\xi\eta}$. Since cross terms are "second generation" effects we consider them only if they are of order S^0 . Thus, $\chi_{\xi\eta,\rho\eta}$ with $\xi\eta$ and $\rho\eta$ not the same combination, is negligible since it has no S^0 term.

d. The $L_{\xi,\eta\rho}$ and $M_{\xi,\eta\rho}$ contributions

These may be derived from the equations of Sections 1.e and 2.e of this Appendix. The results are

$$\sum_{\rho} L_{\rho, \xi\eta} \Lambda^{\rho} = \quad (C-55)$$

$$\begin{aligned} &= (\xi_i \eta_j | u_{ij}^{\xi\eta} v_{ij} (\Lambda^{\xi} v_i^{\xi} + \Lambda^{\eta} v_j^{\eta}) | \xi_i \eta_j) \\ &\quad - (\xi_i \eta_j | u_{ij}^{\xi\eta} v_{ij} | \xi_i \eta_j) \cdot \\ &\quad \cdot [\Lambda^{\xi} (\xi | v^{\xi} | \xi) + \Lambda^{\eta} (\eta | v^{\eta} | \eta)] \\ &\quad - (\xi_i \eta_j | u_{ij}^{\xi\eta} v_{ij} | \xi_i \eta_j) \sum_{\rho} \Lambda^{\rho} (\rho | v^{\rho} | \rho) \end{aligned}$$

$$\sum_{\rho} M_{\rho, \xi\eta} \Lambda^{\rho} = \quad (C-56)$$

$$\begin{aligned} &= (\xi_i \eta_j | u_{ij}^{\xi\eta} v_{ij} (\mathcal{L}^{\xi} \omega_i^{\xi} \underline{L} \cdot \underline{\sigma} + \mathcal{L}^{\eta} \omega_j^{\eta} \underline{L} \cdot \underline{\sigma}) | \xi_i \eta_j) \\ &\quad - (\xi_i \eta_j | u_{ij}^{\xi\eta} v_{ij} | \xi_i \eta_j) \cdot \\ &\quad \cdot [(\xi | \mathcal{L}^{\xi} \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) + (\eta | \mathcal{L}^{\eta} \omega^{\eta} \underline{L} \cdot \underline{\sigma} | \eta)] \\ &\quad - (\xi_i \eta_j | u_{ij}^{\xi\eta} v_{ij} | \xi_i \eta_j) \sum_{\rho} (\rho | \mathcal{L}^{\rho} \omega^{\rho} \underline{L} \cdot \underline{\sigma} | \rho). \end{aligned}$$

To make clearer the calculation of $(\lambda^{\xi\eta} + \lambda^{\eta\xi})$, we shall make a calculation of the S^0 terms. To order S^0 the only terms contributing to $\pi_{\xi\eta}$ come from the first set of terms of Eq. (C-48). The result is

$$\pi_{\xi\eta} = (\xi_i\eta_j | \frac{u_{ij}^{\xi\eta}}{r_{ij}} | \xi_i\eta_j) \quad (C-57a)$$

Here we have neglected terms in the exchange potential as of order S^2 and used the fact that $u_{ij}^{\xi\eta}$ is odd.

Eq. (C-57a) is the electrostatic interaction between the two electrons in the modified state $\langle \phi^{\xi}(r_i) \phi^{\eta}(r_j) u_{ij}^{\xi\eta} |$. This can be put in a more familiar form by adding the quantity

$(\xi_i\eta_j | u_{ij}^{\xi\eta} (\frac{1}{|\underline{R}_I - \underline{R}_J|} - \frac{1}{|\underline{r}_i - \underline{R}_J|} - \frac{1}{|\underline{r}_j - \underline{R}_I|} | \xi_i\eta_j)$ which is zero by the oddness of $u_{ij}^{\xi\eta}$. The resulting expression is just the matrix element of the interaction of two neutral charge distributions, one having its center at $\underline{R}_J$ and the other at $\underline{R}_I$. Provided there is no overlap, this interaction may be expanded in a multipole series. This is essentially the approach used by Buckingham in his study of Van der Waals forces.

If only dipole-dipole interactions are included the expression for $\pi_{\xi\eta}$ becomes

$$\begin{aligned}
\Pi_{\xi\eta} &= (\xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \eta_j) \\
&= \frac{1}{R_0} (\xi_i \eta_j | [\underline{r}_i' \cdot \underline{r}_j' - \\
&\quad - 3 (\underline{r}_i' \cdot \hat{R})(\underline{r}_j' \cdot \hat{R})]^2 | \xi_i \eta_j)
\end{aligned}
\tag{C-57b}$$

where

$$\underline{R} = \underline{R}_I - \underline{R}_J, \quad \underline{r}_i' = \underline{r}_i - \underline{R}_I \quad \text{and} \quad \underline{r}_j' = \underline{r}_j - \underline{R}_J$$

The S^0 terms in $\Upsilon_{\xi\eta}$ are

$$\begin{aligned}
\Upsilon_{\xi\eta} &= \\
&= (\xi_i \eta_j | (\underline{\nabla}_i u_{ij}^{\xi\eta} \cdot \underline{\nabla}_i u_{ij}^{\xi\eta}) + (\underline{\nabla}_j u_{ij}^{\xi\eta} \cdot \underline{\nabla}_j u_{ij}^{\xi\eta}) | \xi_i \eta_j) \\
&\quad + (\xi_i \eta_j | \frac{(u_{ij}^{\xi\eta})^2}{r_{ij}} | \xi_i \eta_j) \\
&\quad - (\xi_i \eta_j \eta_k | \frac{(u_{ij}^{\xi\eta})^2}{r_{ik}} | \xi_i \eta_j \eta_k) \\
&\quad - (\xi_i \eta_j \xi_k | \frac{(u_{ij}^{\xi\eta})^2}{r_{jk}} | \xi_i \eta_j \xi_k) \\
&\quad + (\xi_i \eta_j | (u_{ij}^{\xi\eta})^2 | \xi_i \eta_j) (\xi_i \eta_j | \frac{1}{r_{ij}} | \xi_i \eta_j).
\end{aligned}
\tag{C-58a}$$

Here we have neglected terms in the exchange potential, $\cong \sqrt{\quad}$, since they are of order greater than S^0 and we have used the oddness of $u_{ij}^{\xi\eta}$ to eliminate any contribution from Υ_2 . This can be further simplified by observing that if the interactions between nuclei and

between electrons and nuclei are added and subtracted from the last four terms, these can be made to be the electrostatic interaction between neutral charge clouds. In the dipole approximation this is odd and so to order S^0 using the dipole approximation,

$$\begin{aligned} \mathcal{I}_{\xi\eta,\xi\eta} &= \quad \quad \quad (C-58b) \\ &= \frac{1}{2} (\xi_i\eta_j | \nabla_i u_{ij}^{\xi\eta} \cdot \nabla_i u_{ij}^{\xi\eta} + \nabla_j u_{ij}^{\xi\eta} \cdot \nabla_j u_{ij}^{\xi\eta} | \xi_i\eta_j) \end{aligned}$$

To order S^0 no correction due to Λ should enter since Λ is of order S^2 . Furthermore, the small size of χ , the spin-orbit factor, will make the spin-orbit correction negligible compared with (C-56b) which is of the order of the dipole matrix elements of the charge distributions $|\varphi^3|^2$ and $|\varphi^7|^2$.

APPENDIX D
DETAILS OF THE CALCULATION OF ELECTRON SPIN RESONANCE
PARAMETERS

1. Matrix Elements of the Magnetic Field and Hyperfine Perturbations

The perturbations $h_{h.f.s.}$ and $h_{\underline{H}}$ defined by Eqs. (8-1) and (8-3) respectively are both sums of one-electron operators. The expectation value of these for the crystal wave function (6-6) can be written down by analogy with Eq. (7-4) as

$$\begin{aligned} E = \epsilon' &+ \left\{ [\mu' - \epsilon' \alpha] + [\nu' - \epsilon' \beta - \alpha(\mu' - \epsilon' \alpha)] \right\} \\ &+ \left\{ [M' - \epsilon' A] + [N' - \epsilon' B - A(M' - \epsilon' A)] \right\} \\ &+ \left\{ [m' - \epsilon' a] + [n' - \epsilon' b - a(m' - \epsilon' a)] \right\} \\ &+ \left\{ P'_{\Lambda R} - \epsilon' C_{\Lambda R} - (\alpha M' + A \mu') + 2\alpha A \epsilon' \right\} \\ &+ \left\{ P'_{\Lambda \lambda} - \epsilon' C_{\Lambda \lambda} - (\alpha m' + a \mu') + 2\alpha a \epsilon' \right\} \\ &+ \left\{ P'_{\lambda \lambda} - \epsilon' C_{\lambda \lambda} - (\alpha M' + A m') + 2\alpha A \epsilon' \right\}. \end{aligned}$$

(D-1)

Here the primes indicate that these quantities are of the same form as ϵ , μ , ν , etc. but with the operator $\mathcal{H}'$ replaced by h where h is either $h_{h.f.s.}$ or $h_{\underline{H}}$.

Since we have found Λ to be of order S^2 , the Λ^2 term is not needed in our approximation. The explicit forms for the quantities in Eq. (D-1) are:

$$\epsilon' = \sum_{\xi} \langle \xi | h | \xi \rangle \quad (\text{D-2a})$$

$$\begin{aligned} u' - \epsilon' a &= \\ &= 2 \sum_{\xi} \Lambda^{\xi} \left[\langle \xi | v^{\xi} h | \xi \rangle - \sum_{\eta} \langle \xi | h | \eta \rangle \langle \eta | v^{\xi} | \xi \rangle \right] \quad (\text{D-2b}) \end{aligned}$$

$$\begin{aligned} M' - \epsilon' A &= \\ &= \sum_{\xi} \mathcal{L}^{\xi} \left[\langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\omega} h + h \omega^{\xi} \underline{L} \cdot \underline{\omega} | \xi \rangle - \right. \\ &\quad \left. - \sum_{\eta} \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\omega} | \eta \rangle \langle \eta | h | \xi \rangle \right. \\ &\quad \left. - \sum_{\eta} \langle \xi | h | \eta \rangle \langle \eta | \omega^{\xi} \underline{L} \cdot \underline{\omega} | \xi \rangle \right] \quad (\text{D-2c}) \end{aligned}$$

$$\begin{aligned} m' - \epsilon' a &= \\ &= 2 \sum_{\xi} \sum_{\eta} (\lambda^{\xi \eta} + \lambda^{\eta \xi}) \\ &\quad \cdot \left\{ \langle \xi_i \eta_j | u_{ij}^{\xi \eta} (h_i + h_j) | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | u_{ij}^{\xi \eta} (h_i + h_j) | \eta_i \xi_j \rangle \right. \\ &\quad \left. - [\langle \xi_i \eta_j | u_{ij}^{\xi \eta} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | u_{ij}^{\xi \eta} | \eta_i \xi_j \rangle] \right. \\ &\quad \left. [\langle \xi | h | \xi \rangle + \langle \eta | h | \eta \rangle] \right\} \\ &= \sum_{\substack{\xi \neq \eta \\ \xi, \eta}} 2 \left[\langle \xi_i \eta_j | u_{ij}^{\xi \eta} | \xi_i \eta_j \rangle - \langle \xi_i \eta_j | u_{ij}^{\xi \eta} | \eta_i \xi_j \rangle \right] \langle \xi | h | \xi \rangle \quad (\text{D-2d}) \end{aligned}$$

$$N' - E'B =$$

$$\begin{aligned}
 &= \sum_{\xi} \mathcal{L}^{\xi} \mathcal{L}^{\xi} \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi \rangle - \\
 &\quad - \sum_{\xi} \sum_{\eta} \mathcal{L}^{\xi} \mathcal{L}^{\eta} \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta \rangle \langle \eta | \mathcal{H} | \xi \rangle \\
 &\quad + \sum_{\xi} \sum_{\eta \neq \xi} \mathcal{L}^{\xi} \mathcal{L}^{\eta} \langle \xi | \eta | \omega_i^{\xi} \underline{L} \cdot \underline{\sigma}_i (h_i + h_j) \omega_j^{\eta} \underline{L}_j \cdot \underline{\sigma}_j | \xi | \eta \rangle \\
 &\quad - \mathcal{L}^{\xi} \mathcal{L}^{\xi} \langle \xi | \eta | \omega_i^{\xi} \underline{L} \cdot \underline{\sigma}_i (h_i + h_j) \omega_j^{\xi} \underline{L}_j \cdot \underline{\sigma}_j | \eta | \xi \rangle \\
 &\quad - \sum_{\xi} \sum_{\eta \neq \xi} \sum_{\rho \neq \xi} \left[\mathcal{L}^{\xi} \mathcal{L}^{\rho} \langle \xi | \eta | \omega_i^{\xi} \underline{L} \cdot \underline{\sigma}_i \omega_j^{\rho} \underline{L}_j \cdot \underline{\sigma}_j | \xi | \rho \rangle \right. \\
 &\quad \quad - \mathcal{L}^{\xi} \mathcal{L}^{\xi} \langle \xi | \eta | \omega_i^{\xi} \underline{L} \cdot \underline{\sigma}_i \omega_j^{\xi} \underline{L}_j \cdot \underline{\sigma}_j | \rho | \xi \rangle \left. \right] \langle \rho | \mathcal{H} | \eta \rangle \\
 &\quad + \left[\mathcal{L}^{\xi} \mathcal{L}^{\eta} \langle \xi | \eta | \omega_i^{\xi} \underline{L} \cdot \underline{\sigma}_i \omega_j^{\eta} \underline{L}_j \cdot \underline{\sigma}_j | \rho | \eta \rangle \right. \\
 &\quad \quad \left. - \mathcal{L}^{\xi} \mathcal{L}^{\rho} \langle \xi | \eta | \omega_i^{\xi} \underline{L} \cdot \underline{\sigma}_i \omega_j^{\rho} \underline{L}_j \cdot \underline{\sigma}_j | \eta | \rho \rangle \right] \langle \rho | \mathcal{H} | \xi \rangle \\
 &\quad - \sum_{\xi} \sum_{\eta \neq \xi} \left[\mathcal{L}^{\xi} \mathcal{L}^{\eta} \langle \xi | \eta | \omega_i^{\xi} \underline{L} \cdot \underline{\sigma}_i \omega_j^{\eta} \underline{L}_j \cdot \underline{\sigma}_j | \xi | \eta \rangle \right. \\
 &\quad \quad \left. - \mathcal{L}^{\xi} \mathcal{L}^{\xi} \langle \xi | \eta | \omega_i^{\xi} \underline{L} \cdot \underline{\sigma}_i \omega_j^{\xi} \underline{L}_j \cdot \underline{\sigma}_j | \eta | \xi \rangle \right] \\
 &\quad \cdot [\langle \xi | \mathcal{H} | \xi \rangle + \langle \eta | \mathcal{H} | \eta \rangle]
 \end{aligned}$$

(D-2e)

$$A(M' - E'A) =$$

$$\begin{aligned}
 &= 2 \sum_{\xi} \sum_{\rho} \mathcal{L}^{\xi} \mathcal{L}^{\rho} \langle \rho | \omega^{\rho} \underline{L} \cdot \underline{\sigma} | \rho \rangle \\
 &\quad \cdot \{ \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi \rangle + \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta \rangle \langle \eta | \mathcal{H} | \xi \rangle \} \\
 &\quad - \sum_{\eta} 2 \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta \rangle \langle \eta | \mathcal{H} | \xi \rangle \}
 \end{aligned}$$

(D-2f)

$$(m' - \epsilon' b) =$$

$$\begin{aligned}
 &= \sum_{\xi} \sum_{\eta} (\lambda^{\xi\eta} + \lambda^{\eta\xi})^2 \left\{ \langle \xi; \eta_j | u_{ij}^{\xi\eta} (h_i + h_j) u_{ij}^{\xi\eta} | \xi; \eta_j \rangle \right. \\
 &\quad - \langle \xi; \eta_j | u_{ij}^{\xi\eta} (h_i + h_j) u_{ij}^{\xi\eta} | \eta; \xi_j \rangle \\
 &\quad - \left[\langle \xi; \eta_j | (u_{ij}^{\xi\eta})^2 | \xi; \eta_j \rangle - \langle \xi; \eta_j | u_{ij}^{\xi\eta} u_{ij}^{\eta\xi} | \eta; \xi_j \rangle \right] \\
 &\quad \cdot [\langle \xi | h | \xi \rangle + \langle \eta | h | \eta \rangle] \\
 &\quad - 2 \sum_{\substack{p \neq \xi \\ \neq \eta}} (\lambda^{\xi\eta} + \lambda^{\eta\xi}) (\lambda^{p\eta} + \lambda^{\eta p}) \langle p | h | \xi \rangle \\
 &\quad \cdot [\langle \xi; \eta_j | u_{ij}^{\xi\eta} u_{ij}^{p\eta} | p; \eta \rangle - \langle \xi; \eta_j | u_{ij}^{\xi\eta} u_{ij}^{p\eta} | \eta; p_j \rangle] \Big\} \\
 &\hspace{15em} (D-2g)
 \end{aligned}$$

$$\begin{aligned}
 \alpha (m' - \epsilon' a) &= 2 \sum_{\rho} \sum_{\sigma} (\lambda^{\rho\sigma} + \lambda^{\sigma\rho}) \\
 &\quad \cdot [\langle \rho; \sigma_j | u_{ij}^{\rho\sigma} | \rho; \sigma_j \rangle - \langle \rho; \sigma_j | u_{ij}^{\rho\sigma} | \sigma; \rho_j \rangle] (m' - \epsilon' a) \\
 &\hspace{15em} (D-2h)
 \end{aligned}$$

$$\begin{aligned}
 P'_{\Lambda\mathcal{L}} - C'_{\Lambda\mathcal{L}} - (\alpha M' + A \mu') + 2\alpha A \epsilon' &= \\
 &= \sum_{\xi} \Lambda^{\xi} \mathcal{L}^{\xi} \langle \xi | v^{\xi} h \omega^{\xi} \underline{h} \cdot \underline{\omega} | \xi \rangle \\
 &\quad - \sum_{\xi} \sum_{\eta} \Lambda^{\xi} \mathcal{L}^{\eta} \langle \xi | v^{\xi} \omega^{\eta} \underline{h} \cdot \underline{\omega} | \eta \rangle \langle \eta | h | \xi \rangle \\
 &\quad - \sum_{\xi} \sum_{\eta} \Lambda^{\xi} \mathcal{L}^{\xi} \langle \xi | v^{\xi} | \eta \rangle \langle \eta | h \omega^{\xi} \underline{h} \cdot \underline{\omega} | \xi \rangle \\
 &\quad - \sum_{\xi} \sum_{\eta} \Lambda^{\xi} \mathcal{L}^{\xi} \langle \xi | v^{\xi} h | \eta \rangle \langle \eta | \omega^{\xi} \underline{h} \cdot \underline{\omega} | \xi \rangle
 \end{aligned}$$

$$\begin{aligned}
& + \sum_{\xi} \sum_{\eta} \sum_{\rho} \Lambda^{\xi} \mathcal{L}^{\xi} \langle \xi | v^{\xi} | \rho \rangle \langle \eta | \omega^{\xi} \underline{L} \cdot \underline{\omega} | \xi \rangle \langle \rho | h | \eta \rangle \\
& + \sum_{\xi} \sum_{\eta} \sum_{\rho} \Lambda^{\xi} \mathcal{L}^{\rho} \langle \xi | v^{\xi} | \eta \rangle \langle \eta | \omega^{\rho} \underline{L} \cdot \underline{\omega} | \rho \rangle \langle \rho | h | \xi \rangle
\end{aligned}$$

+ transpose .

(D-21)

$$\begin{aligned}
P'_{\Lambda\lambda} - \epsilon' C_{\Lambda\lambda} - (\alpha m' + a u') + 2\alpha a \epsilon' = \\
= - \sum_{\xi} \sum_{\eta} \sum_{\rho} (\lambda^{\xi\eta} + \lambda^{\eta\xi}) \left[\Lambda^{\xi} \langle \xi | \eta_j | u_{ij}^{\xi\eta} \rangle h_{ij} | \xi_i \rho_j \rangle \langle \rho | v^{\eta} | \eta \rangle \right. \\
\left. + \Lambda^{\xi} \langle \xi | \eta_j | u_{ij}^{\xi\eta} \rangle h_{ij} | \rho_i \eta_j \rangle \langle \eta | v^{\xi} | \xi \rangle \right] \\
+ \text{transpose}
\end{aligned}$$

(D-2j)

+ other terms that are zero to order S^2 by the oddness of $u_{ij}^{\xi\eta}$ and the spherical symmetry of v^{ξ} .

Here we have written terms involving $\omega^{\xi} \underline{L} \cdot \underline{\omega} h$ and $h \omega^{\xi} \underline{L} \cdot \underline{\omega}$ separately, since h and $\underline{L} \cdot \underline{\omega}$ may not commute (see Section 1.a of Appendix C for such a case). We have also omitted the $\mathcal{L} \lambda$ cross term since it is of exactly the same form as the $\Lambda \lambda$ term.

2. The Magnetic Field Interaction

The operator is:

$$h_{\underline{H}}(\underline{r}_i) = \beta \left(\underline{L}_i + \frac{q}{2} \underline{\sigma} \right) \cdot \underline{H} \quad (\text{D-3})$$

First we note that the Löwdin wave functions or any wave functions orthogonalized by a similar method are spin eigenfunctions provided the initial set of atomic wave functions are spin eigenfunctions. This follows because in orthogonalizing a wave function to others in the set of starting functions, wave functions that overlap are subtracted out and only those wave functions with the same spin overlap, the result being a linear combination of the initial wave functions all with the same spin part.

a. The constant term, ϵ'

The part of the expectation value linear in $\underline{H}$ and $\underline{\sigma}$ is

$$\epsilon' = \sum_{\nu} \langle \nu | \beta \frac{q}{2} \underline{\sigma} \cdot \underline{H} | \nu \rangle \quad (\text{D-4})$$

The sum over ν will be zero for the paired spin states arising from the argon atoms, leaving only the unpaired spin of the hydrogen atom to give

$$\epsilon' = \frac{q}{2} \beta \underline{H} \cdot (0 | \underline{\sigma} | 0) \quad (\text{D-5})$$

Here $\nu = 0$ denotes the hydrogen 1s state. This simply states the fact that a unitary transformation does not

change the net spin of a set of wave functions.

b. The Λ , λ , λ^2 and $\lambda\Lambda$ terms

These make no contribution to the g factor.

This may be seen as follows. Since we seek that part of the expectation value proportional to $\underline{H}$ and $\underline{Q}$ and neither v^z nor $u_{ij}^{\xi\eta}$ contain the spin operator, we need only consider the spin part of the magnetic field interaction.

The Λ contribution has the form

$$\sum_{\xi} \Lambda^{\xi} \left\{ \langle \xi | v^{\xi} h | \xi \rangle - \sum_{\eta} \langle \xi | v^{\xi} | \eta \rangle \langle \eta | h | \xi \rangle \right\}, \quad (D-6)$$

while the λ , λ^2 and $\Lambda\lambda$ contributions have two types of terms. Specifically for the λ contribution they are:

(1)

$$\begin{aligned} & \langle \xi_i \eta_j | u_{ij}^{\xi\eta} (h_i + h_j) | \xi_i \eta_j \rangle - \\ & - \langle \xi_i \eta_j | u_{ij}^{\xi\eta} | \xi_i \eta_j \rangle [\langle \xi | h | \xi \rangle + \langle \eta | h | \eta \rangle] \end{aligned} \quad (D-7)$$

or the exchange with ξ and η reversed in the ket, and

(2)

$$\sum_{\substack{p \neq \xi \\ p \neq \eta}} [\langle \xi_i \eta_j | u_{ij}^{\xi\eta} | p_i \eta_j \rangle - \langle \xi_i \eta_j | u_{ij}^{\xi\eta} | \eta_i p_j \rangle] \langle p | h | \xi \rangle. \quad (D-8)$$

The λ^2 contribution has the same form as the λ except that an extra u_{ij}^{57} appears in some of the matrix elements. The same holds for the $\wedge \lambda$ term but with extra v^3 's.

Now, since we consider $h = \frac{g}{2} \beta \underline{\sigma} \cdot \underline{H}$, we can take the expectation value of $\underline{\sigma}$ outside the matrix elements in terms like (D-6) and (D-7). The non-angular parts then cancel identically. Furthermore, in terms of type (D-8), ρ is never equal to ξ and so $\langle \varphi | \underline{\sigma} | \xi \rangle \cdot \underline{H}$ is zero by orthogonality.

c. The $\mathcal{L}$ term

Since the operator $\omega^\xi \underline{L} \cdot \underline{\sigma}$ is not diagonal, it mixes spin and angular momentum states. We must therefore consider both $\underline{L}$ and $\underline{\sigma}$ parts of the interaction with the magnetic field. The operator in the first part of Eq. (D-2c) simplifies when we use the assumption that ω^ξ is an s-like function. Then,

$$\begin{aligned} \omega^\xi \underline{L} \cdot \underline{\sigma} \hbar_H + \hbar_H \omega^\xi \underline{L} \cdot \underline{\sigma} &= \\ &= \beta \omega^\xi [(\underline{\sigma} \cdot \underline{L} \underline{L} \cdot \underline{H} + \underline{H} \cdot \underline{L} \underline{L} \cdot \underline{\sigma}) \\ &\quad + \frac{g}{2} (\underline{L} \cdot \underline{\sigma} \underline{H} \cdot \underline{\sigma} + \underline{H} \cdot \underline{\sigma} \underline{L} \cdot \underline{\sigma})] \\ &= \beta \omega^\xi [\underline{\sigma} \cdot \underline{L} \cdot \underline{H} + \frac{g}{2} \underline{L} \cdot \underline{H}], \end{aligned}$$

(D-9)

where $\hat{\Pi}$ is the dyadic $\hat{\Pi} = \hat{i} [L_i L_j + L_j L_i] \hat{j}$ $i, j = \hat{x}, \hat{y}, \hat{z}$

The second term was obtained by using the equation

$\underline{A} \cdot \underline{\sigma} \underline{B} \cdot \underline{\sigma} = \underline{A} \cdot \underline{B} + i \underline{\sigma} \underline{A} \times \underline{B}$ due to Dirac. The first factor will contribute to the g factor since it is linear in $\underline{H}$ and $\underline{\sigma}$, but the second term will not.

Using the results of Appendix B to transform the $\mathcal{L}$ contribution of Eq. (D-9), we have

(D-10)

$$\begin{aligned}
 M' - \epsilon' A = & \sum_{\xi} \mathcal{L}^{\xi} \left\{ (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} h_H + h_H \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) (1 + \frac{3}{4} \sum_{\beta} S_{\xi\beta}^2) \right. \\
 & - \sum_{\alpha} S_{\xi\alpha} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} h_H + h_H \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \alpha) \\
 & + \frac{3}{4} \sum_{\alpha \neq \xi} \sum_{\beta} S_{\alpha\beta} S_{\beta\xi} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} h_H + h_H \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \alpha) \\
 & \left. + \frac{1}{4} \sum_{\alpha} \sum_{\beta} S_{\alpha\xi} S_{\beta\xi} (\alpha | \omega^{\xi} \underline{L} \cdot \underline{\sigma} h_H + h_H \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \beta) \right\} \\
 & - \sum_{\xi} \sum_{\eta} \mathcal{L}^{\xi\eta} \left\{ [(\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | h_H | \xi) (1 + \frac{3}{4} \sum_{\alpha} S_{\alpha\xi}^2 + \frac{3}{4} \sum_{\alpha} S_{\alpha\eta}^2) \right. \\
 & \sum_{\alpha \neq \xi} (-\frac{1}{2} S_{\alpha\xi} + \frac{3}{8} \sum_{\beta} S_{\alpha\beta} S_{\beta\xi}) \cdot \\
 & [(\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | h_H | \alpha) + (\alpha | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | h_H | \xi)] \\
 & \sum_{\alpha \neq \eta} (-\frac{1}{2} S_{\alpha\eta} + \frac{3}{8} \sum_{\beta} S_{\alpha\beta} S_{\beta\eta}) \cdot \\
 & [(\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \alpha) (\eta | h_H | \xi) + (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\alpha | h_H | \xi)] \\
 & + \frac{1}{4} \sum_{\alpha} \sum_{\beta} S_{\alpha\eta} S_{\beta\xi} [(\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \alpha) (\eta | h_H | \beta) + \\
 & + (\beta | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \alpha) (\eta | h_H | \xi) + (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\alpha | h_H | \beta) + \\
 & \left. + (\beta | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) (\alpha | h_H | \xi)] \right\} \\
 & + \frac{1}{4} \sum_{\alpha} \sum_{\beta} S_{\alpha\xi} S_{\beta\xi} (\alpha | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | h_H | \beta) \\
 & + \frac{1}{4} \sum_{\alpha} \sum_{\beta} S_{\alpha\eta} S_{\beta\eta} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \alpha) (\beta | h_H | \xi) + \text{transpose} \left. \right\} .
 \end{aligned}$$

For $\zeta = 0$, the hydrogen 1s state, this simplifies considerably. Since we need be concerned only with the $\underline{L}$ part of $\underline{h}_H$, as shown above, and there is another $\underline{L}$ in the variation, most of the terms are zero. The result is

$$\begin{aligned} \frac{\beta}{4} \mathcal{L}^0 \sum_{\alpha} \sum_{\beta} S_{\alpha,0} S_{\beta,0} \cdot \\ \cdot \left\{ (\alpha | \omega^0 (\underline{H} \cdot \underline{L} \underline{L} \cdot \underline{\sigma} + \underline{\sigma} \cdot \underline{L} \underline{L} \cdot \underline{H}) | \beta) \right. \\ \left. - \sum_{\eta} (\alpha | \underline{H} \cdot \underline{L} | \eta) (\eta | \omega^0 \underline{L} \cdot \underline{\sigma} | \beta) \right. \\ \left. - \sum_{\eta} (\alpha | \omega^0 \underline{L} \cdot \underline{\sigma} | \eta) (\eta | \underline{L} \cdot \underline{H} | \beta) \right\} \quad (D-11) \end{aligned}$$

Now η runs over all atomic functions in the crystal. In particular, to order S^2 , when φ^{α} and φ^{β} are centered on the same atom, η runs over all the functions on that same center. Let us write the wave functions symbolically as $\varphi^{\alpha} = R^{\alpha} Y^{\alpha} \delta(\alpha)$ where R^{α} is the radial part with quantum number n_{α} and $Y^{\alpha} \delta(\alpha)$ the spin-angular part with quantum numbers $\ell_{\alpha}, m_{\alpha}$ and σ_{α} . The second line then becomes

(D-12)

$$\begin{aligned} \sum_{\eta} (\alpha | \underline{H} \cdot \underline{L} | \eta) (\eta | \omega^0 \underline{L} \cdot \underline{\sigma} | \beta) = \\ \sum_{\eta} (R^{\alpha} | R^{\eta}) (R^{\eta} | \omega^0 | R^{\beta}) \\ \cdot (Y^{\alpha} \delta(\alpha) | \underline{H} \cdot \underline{L} | Y^{\eta} \delta(\eta)) (Y^{\eta} \delta(\eta) | \underline{L} \cdot \underline{\sigma} | Y^{\alpha} \delta(\alpha)). \end{aligned}$$

The first factor is $(R^\alpha | R^\eta) = \delta_{\alpha, \eta}$; so that α and η must belong to the same subshell. Furthermore, the sum over the angular functions within a subshell reduces the last two terms:

$$\begin{aligned} \sum_{\eta} (Y^\alpha_{\delta(\alpha)} | \underline{H} \cdot \underline{L} | Y^\eta_{\delta(\eta)}) (Y^\eta_{\delta(\eta)} | \underline{L} \cdot \underline{\sigma} | Y^\beta_{\delta(\beta)}) &= \quad (D-13) \\ &= (Y^\alpha_{\delta(\alpha)} | \underline{H} \cdot \underline{L} \underline{L} \cdot \underline{\sigma} | Y^\beta_{\delta(\beta)}) \end{aligned}$$

Thus the second line of Eq. (D-11) becomes

$(\alpha | \omega^3 \underline{H} \cdot \underline{L} \underline{L} \cdot \underline{\sigma} | \beta)$ and cancels the first half of the first line. The third line may be treated similarly and is found to cancel the second half of the first line. The contribution to the g factor from the admixture of p state to the hydrogen 1s function is therefore zero to order S^2 in the Löwdin scheme of orthonormalization.

For $\sum$ an argon s function, there is no contribution since there is no spin-orbit interaction in s states. However, for $\sum$ an argon p function there is a contribution. In this case Eq. (D-10) simplifies when the argon-argon overlaps are neglected. The result is

$$M' - \epsilon' A =$$

$$\begin{aligned}
&= \beta \sum_{\substack{\xi \\ \text{non-zero}}} \mathcal{L}^{\xi} \left\{ (\xi | \omega^{\xi} (\underline{\sigma} \cdot \underline{L} \underline{L} \cdot \underline{H} + \underline{H} \cdot \underline{L} \underline{L} \cdot \underline{\sigma}) | \xi) \right. \\
&\quad \cdot (1 + \frac{3}{4} S_{\xi 0}^2) \\
&\quad + \frac{3}{4} \sum_{\alpha \neq \xi} \sum_{\beta} S_{\alpha 0} S_{\beta 0} (\xi | \omega^{\xi} (\underline{\sigma} \cdot \underline{L} \underline{L} \cdot \underline{H} + \underline{H} \cdot \underline{L} \underline{L} \cdot \underline{\sigma}) | \alpha) \\
&\quad - \left[\sum_{\substack{\eta \\ \text{non-zero}}} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | \underline{L} \cdot \underline{H} | \xi) (1 + \frac{3}{4} S_{\xi}^2 + \frac{3}{4} S_{0\eta}^2) \right. \\
&\quad + \frac{3}{8} \sum_{\alpha \neq \xi} S_{\alpha 0} S_{0\xi} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | \underline{L} \cdot \underline{H} | \alpha) \\
&\quad + S_{\alpha 0} S_{0\xi} (\alpha | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\eta | \underline{L} \cdot \underline{H} | \xi) \\
&\quad + \frac{3}{8} \sum_{\alpha \neq \eta} S_{\alpha 0} S_{0\eta} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \alpha) (\eta | \underline{L} \cdot \underline{H} | \xi) \\
&\quad + S_{\alpha 0} S_{0\eta} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta) (\alpha | \underline{L} \cdot \underline{H} | \xi) \\
&\quad + \frac{1}{4} \sum_{\alpha} \sum_{\beta} S_{\alpha 0} S_{\beta 0} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \alpha) \\
&\quad \cdot (\beta | \underline{L} \cdot \underline{H} | \xi) \\
&\quad \left. + \text{transpose} \right\} \quad (D-14)
\end{aligned}$$

On applying the sum rule to the first and third and the second and fourth terms we are left with

$$\begin{aligned}
& -\beta \sum_{\substack{\xi \\ \text{non-zero}}} \mathcal{L}^{\xi} \left\{ \sum_{\alpha} \sum_{\beta} S_{\alpha 0} S_{0\beta} (\alpha | \underline{\sigma} \cdot \underline{L} | \xi) (\xi | \omega^{\xi} \underline{L} \cdot \underline{H} | \beta) \right. \\
&\quad \left. + \text{transpose} \right\} \\
& \quad (D-15)
\end{aligned}$$

Here we have combined the last three terms by relabeling

the wave functions. Applying the sum rule to the sum over ξ we have, since α and ξ must belong to the same subshell, and $\mathcal{L}^\xi$ is a constant for a given subshell,

$$\begin{aligned} M' - \epsilon' A &= \frac{\beta}{2} \sum_{\alpha} \sum_{\xi} \mathcal{L}^{\alpha} S_{\alpha 0} S_{\xi 0} (\alpha | \omega^{\alpha} \mathbf{r} \cdot \mathbf{r} \cdot \mathbf{H} | \beta) \\ &= -\beta \sum_{\alpha} \sum_{\xi} \mathcal{L}^{\alpha} S_{\alpha 0} S_{\xi 0} (\alpha | \omega^{\alpha} \mathbf{r} \cdot \mathbf{r} \cdot \mathbf{H} | \beta) \end{aligned} \quad (\text{D-16})$$

d. The $\mathcal{L}^2$ term

This term and the $\mathcal{L}$ and $\mathcal{L}^\lambda$ terms of the next section (2.e) are of second order in the variational parameters. Since the matrix elements of the variational corrections are small, these terms are of second order of smallness to start with and so we shall only consider S^0 terms. A calculation similar to that of Section 2.c of this appendix may be made for the $\mathcal{L}^2$ contribution using Eqs. (D-2e) and (D-2f). However, from the form of the first four terms of Eq. (D-2e) it is clear that to order S^0 any contributions will vanish identically as the S^0 term did for the $\mathcal{L}$ contribution. The remaining terms will be zero by orthogonality. The second part of the $\mathcal{L}^2$ term of Eq. (D-2f) is zero to order S^0 since $M' - \epsilon' A$ is zero to order S^0 .

e. The $\mathcal{L}$ and $\mathcal{L}^\lambda$ terms

To order S^0 these are zero by the same argument

as for the $\mathcal{L}^2$ terms, the terms either cancelling because of the "sum rule" or vanishing because of orthogonality of the wave functions.

3. The Hyperfine Interaction

The operator is

$$\begin{aligned}
 h_{\text{h.f.s.}} = & 2 \sum_{\mathbf{J}} \delta_{\mathbf{J}} \beta_e \beta_n \cdot \\
 & \cdot \sum_i \left\{ \frac{(L_i - \frac{3}{4} \underline{\sigma})}{|\underline{r}_i - \underline{R}_{\mathbf{J}}|^3} \cdot \underline{I}_{\mathbf{J}} + \right. \\
 & + \frac{3g}{4} \cdot \frac{(\underline{r}_i - \underline{R}_{\mathbf{J}}) \cdot \underline{\sigma} (\underline{r}_i - \underline{R}_{\mathbf{J}}) \cdot \underline{I}_{\mathbf{J}}}{|\underline{r}_i - \underline{R}_{\mathbf{J}}|^5} \\
 & \left. + \frac{4\pi g}{3} \delta(\underline{r}_i - \underline{R}_{\mathbf{J}}) \frac{\underline{\sigma}}{2} \cdot \underline{I}_{\mathbf{J}} \right\}
 \end{aligned} \tag{D-17}$$

In most cases it is necessary to consider only the isotropic contact part of this interaction. The symmetry of the trapping sites causes the other terms to cancel identically. The exception is in the $\mathcal{L}$ contribution where the $\underline{L}$ term gives an S^3 term.

a. The constant term, ϵ'

When expanded in atomic functions according to Appendix B, ϵ' becomes

(D-18)

$$\epsilon' = \sum_{\nu} (1 + \sum_{\alpha} S_{\nu\alpha}^2) (\nu | h_{hfs.} | \nu) \\ - \sum_{\mu} S_{\mu\nu} (\nu | h_{hfs.} | \mu) + \sum_{\mu \neq \nu} \sum_{\alpha} S_{\mu\nu} S_{\alpha\nu} (\nu | h_{hfs.} | \mu)$$

The term $(\nu | h_{hfs.} | \nu)$ is non-zero for argon functions, but since their spins and angular momenta are paired the sum is zero; the only contribution coming from the hydrogen's unpaired spin. In the second term either ν or μ must be a hydrogen function, otherwise the term sums to zero as above. When either ν or μ is a hydrogen 1s state, the overlap integral is non-zero only for argon atoms of the same spin as the hydrogen and we have a contribution proportional to $S_{\mu,0} (0 | \delta(r) | \mu)$ or its complex conjugate. The third term is of order S^3 since, by our assumption that argon-argon overlaps may be neglected, ν and μ must both be argon functions and the matrix element of the interaction with the hydrogen nucleus between ν and μ is then of order S .

The final expression is

$$\epsilon'_{hfs.} = \frac{4\pi g}{3} \delta\beta_e \beta_n \underline{I} \cdot (0 | \underline{\sigma} | 0) \cdot \\ \cdot \left[(1 + \sum_{\alpha} S_{\alpha\alpha}^2) (0 | \delta(\underline{r} - \underline{R}_H) | 0) \right. \\ \left. - 2 \sum_{\mu} S_{\mu 0} (0 | \delta(\underline{r} - \underline{R}_H) | \mu) \right] \quad (D-19)$$

where the notation "0" represents the hydrogen 1s state centered at $\underline{r} = \underline{R}_H$.

b. The Λ term

This contribution is of order S^2 and is given by

$$\begin{aligned} \mu' - \epsilon' \alpha = & + \frac{8\pi q}{3} \gamma_{\beta_e \beta_n} \underline{I} \cdot (01 \underline{\sigma} | 0) \Lambda^0 \cdot \\ & [(01 \nu^0 \delta(\underline{r} - \underline{R}_H) | 0) \\ & - (01 \nu^0 | 0) (01 \delta(\underline{r} - \underline{R}_H) | 0)]. \end{aligned} \quad (D-20)$$

The first part is zero since the variation $\nu^0 = \nu^n$ is zero at the hydrogen nucleus. However the second term contributes yielding

$$\begin{aligned} \mu' - \epsilon' \alpha = & - \frac{8\pi q}{3} \gamma_{\beta_e \beta_n} \underline{I} \cdot (01 \underline{\sigma} | 0) \Lambda^0 \quad (D-21) \\ & (01 \nu^0 | 0) (01 \delta(\underline{r} - \underline{R}_H) | 0). \end{aligned}$$

If the crystal field variational function, ν^3 , had been taken to include a non-s angular part, for example a term with cubic symmetry such as $\nu_{4,0}(\underline{r}) Y_4^0 + \nu_{4,4}(\underline{r}) (Y_4^4 + Y_4^{-4})$, the $\frac{\underline{L} \cdot \underline{r}}{r^3}$ term would have entered. However, it would appear in order Λ^2 where both the bra and the ket would have contained the Y_4 's. Since we have found that, in molecular crystals Λ is of order S^2 , any such non-s contribution

would appear to be negligible.

c. The $\mathcal{L}$ term

This makes no contribution to the hyperfine interaction through the contact term. The $\mathcal{L}$ term is from Eq. (D-2c)

$$\begin{aligned}
 (M' - \epsilon' A)_{\text{contact}} &= \\
 &= \sum_{\xi} \mathcal{L}^{\xi} \left\{ \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} h_{\text{hfs}} + h_{\text{hfs}} \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi \rangle \right. \\
 &\quad - \sum_{\eta} \langle \xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \eta \rangle \langle \eta | h_{\text{hfs}} | \xi \rangle \\
 &\quad \left. - \sum_{\eta} \langle \xi | h_{\text{hfs}} | \eta \rangle \langle \eta | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi \rangle \right\}.
 \end{aligned}
 \tag{D-22}$$

Now with $h_{\text{hfs}} \sim \underline{I} \cdot \underline{\sigma} \delta(\underline{r} - \underline{R}_H)$, the operator in the first term becomes $\omega^{\xi} \delta(\underline{r} - \underline{R}_H) \underline{L} \cdot \underline{\sigma}$ except for constants.

When the Löwdin functions are expanded into atomic ones, we find that this is zero for the hydrogen ground state and sums to zero for the closed-shell argon functions.

On expansion of the second and third terms to order S^2 it is found that most terms vanish either because of the sum over argon states or because the hydrogen is in an S state. However, some S^2 terms like

$$\sum_{\xi} S_{0\xi} (\xi | \omega^{\xi} \underline{L} \cdot \underline{\sigma} | \xi) (\xi | \delta(\underline{r} - \underline{R}_H) \underline{I} \cdot \underline{\sigma} | 0)
 \tag{D-23}$$

remain. Since $S_0 \zeta$ is non-zero only for ζ states, the sum over ζ in the first matrix element is zero for a symmetric site.

The $\underline{L}/r^3$ part of the hyperfine interaction does not contribute to order S^2 either. When simplified by the Dirac identity we have

$$\begin{aligned}
 (M' - \epsilon' A)_{\text{Angular Momentum}} = & \\
 = 2 \gamma \beta_e \beta_n \sum_{\zeta \neq 0} \mathcal{L}^{\zeta} \left\{ \langle \zeta | \frac{\omega^{\zeta}}{r^3} \underline{\sigma} \cdot \underline{\Gamma} \cdot \underline{I} | \zeta \rangle - \right. & \\
 - \sum_{\eta} \left[\langle \zeta | \omega^{\zeta} \underline{L} \cdot \underline{\sigma} | \eta \rangle \langle \eta | \frac{\underline{L} \cdot \underline{I}}{r^3} | \zeta \rangle \right. & \\
 \left. \left. + \langle \zeta | \frac{\underline{L} \cdot \underline{I}}{r^3} | \eta \rangle \langle \eta | \omega^{\zeta} \underline{L} \cdot \underline{\sigma} | \zeta \rangle \right] \right\} & \quad (D-24)
 \end{aligned}$$

For ζ a hydrogen 1s function, most of the matrix elements are zero as in the case of the g-shift calculation, the only contribution being one proportional to S^2 and having matrix elements like $(\alpha | \frac{Q}{|\underline{r} - \underline{R}_H|^3} | \beta)$ where α and β are argon functions and Q an operator. Since the $\frac{1}{|\underline{r} - \underline{R}_H|^3}$ term is centered on the hydrogen site we neglect such contributions as being of order S^3 .

For ζ an argon function, we find on expansion in atomic functions that the sum over spin-up and spin-down states of the argon closed shells makes S^0 contributions

vanish, while terms with S^2 coefficients are of order S^3 as in the case of φ^3 , a hydrogen 1s function.

d. The λ term

Because of the oddness of $u_{ij}^{\xi\eta}$ and the fact that $u_{ij}^{\xi\eta}$ is zero at the sites on which φ^3 and φ^7 are centered, the λ term gives only exchange contributions to the hyperfine splitting. On expanding Eq. (D-2d) to order S^2 we have

$$\begin{aligned}
 (m' - \epsilon' a) = & \frac{8\pi g}{3} \delta\beta_e \beta_n \underline{I} \cdot (0|\underline{\omega}|0) \cdot \\
 & \sum_{\eta < \gamma} (\lambda^{\eta\gamma} + \lambda^{\gamma\eta}) \left\{ - (0|\eta_j| u_{ij}^{\eta\gamma} \delta(\underline{r}_j - \underline{R}_H) |\gamma_i \sigma_j) \right. \\
 & \quad + \left[(0|\eta_j| u_{ij}^{\eta\gamma} |\gamma_i \sigma_j) - \sum_{\alpha \neq \gamma}^{\epsilon\eta} S_{\alpha 0} (0|\eta_j| u_{ij}^{\eta\alpha} |0_i \alpha_j) \right] \\
 & \quad \cdot (0|\delta(\underline{r} - \underline{R}_H)|0) \left. \right\}
 \end{aligned}
 \tag{D-25}$$

where the symbol $\sum_{\alpha \neq \eta}^{\epsilon\eta}$ indicates the sum over η where η and α are on the same atom but are not the same function.

e. The λ^2 term

This is the renormalization correction due to the addition of the $u^{\xi\eta}$ part of the wave function. In Eq. (D-2g) the first term is zero because of the delta

function in the hyperfine interaction. The next term gives the only contribution,

$$\begin{aligned}
 m' - e'a &= \\
 &= - \frac{4\pi q}{3} \gamma \beta_e \beta_n \underline{I} \cdot (0|\underline{\sigma}|0) \\
 &\quad \sum_{\alpha, \gamma} (\lambda^{\alpha\gamma} + \lambda^{\gamma\alpha})^2 (a; \gamma_j | (u_{ij}^{\alpha\gamma})^2 | a; \gamma_j) (0|\delta(\underline{r}-\underline{R}_H)|0)
 \end{aligned}
 \tag{D-26}$$

the third term and Eq. (D-2h) being of order S^2 .

f. The $\Lambda \mathcal{L}$, $\mathcal{L} \lambda$ and $\Lambda \lambda$ terms

These give no S^0 contribution. The terms involving λ vanish because of the oddness of $u_{ij}^{\lambda\gamma}$ and the fact that it is zero where the δ function is non-zero. The terms in $\mathcal{L}$ vanish to order S^0 by arguments similar to those for the $\mathcal{L}$ term.

APPENDIX E

SUMMARY OF ADRIAN'S CALCULATIONS

To treat the problem of an isolated hydrogen atom in a rare gas solid, Adrian considers the simple product of one-electron wave functions for the crystal. To approximately satisfy the Pauli principle he orthogonalizes the wave function of the hydrogen electron to those of the crystal by the Schmidt process. The predictions of hyperfine splitting and g-shifts are then made by perturbation theory.

He considers the Hamiltonian:

$$\mathcal{H} = \mathcal{H}_H + \mathcal{H}_m + \mathcal{H}_V + \mathcal{H}_{hfs} + \mathcal{H}_{L \cdot S} + \mathcal{H}_{Hfield}$$

where

$\mathcal{H}_H$ is the Hamiltonian for the isolated hydrogen atom

$\mathcal{H}_m$ is the Hamiltonian for the isolated "Matrix",

i.e., crystal atom

$\mathcal{H}_V$ is "The electrostatic interaction between H atom and the 'matrix' atoms."

$$\mathcal{H}_{hfs} = \frac{8\pi}{3} g\beta \left(\frac{\mu_I}{I_H} \right) \delta(\vec{r}) \vec{I}_H \cdot \vec{S}$$

$$\mathcal{H}_{L \cdot S} = \frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} \vec{L} \cdot \vec{S}$$

Here $S = \frac{1}{2} \hbar$

and $L = -i \hbar \vec{r} \times \nabla$

$$\mathcal{H}_{Hfield} = -\frac{e\hbar}{2mc} \vec{H} \cdot (\vec{L} + g\vec{S})$$

He first treats the part $\mathcal{H}_H + \mathcal{H}_m + (\mathcal{H}_V + \mathcal{H}_{hfs})$ where $\mathcal{H}_V + \mathcal{H}_{hfs}$ is considered as the perturbation and then seeks terms in the perturbation expansion that are linear in $\mathcal{H}_{hfs}$, i.e., terms that look like

$$E_{hfs} = \quad (E-1)$$

$$= \langle \psi_{hydrogen1s} | \mathcal{H}_{hfs} | \psi_{hydrogen1s} \rangle [1 + \text{Correction}]$$

Approximating $\mathcal{H}_V$ by a multipole series through dipole quadrupole terms, odd moments occur in all terms so we have the "selection rule"

$$(\psi_0 m_0 | \mathcal{H}_V | \psi_i m_i) = 0 \quad (E-2)$$

if ψ_i is an s state,

where ψ_0 = the atomic wave function for the hydrogen ground state

ψ_0 = the atomic wave function for "matrix" atom ground states.

The subscript i is the index for excited states.

The first-order perturbation result gives the free hydrogen hyperfine splitting:

$$E' = (\psi_0 | \mathcal{H}_{hfs} | \psi_0) \quad (E-3)$$

The second-order term, when the usual sum rule is used, gives:

* In this appendix Adrian's notation is used in most formulas.

$$E^2 = \frac{(\hbar_0 m_0 | \mathcal{H}_{hfs}^2 + 2 \mathcal{H}_{hfs} \mathcal{H}_v + \mathcal{H}_v^2 | \hbar_0 m_0)}{(E_0 - E_i)} \quad (E-4)$$

However, since $\mathcal{H}_v$ is odd this gives no change in the hyperfine interaction energy. The third-order term is given by

$$E^3 = \sum_{i,j}' \sum_{k,l}' \frac{(\hbar_0 m_0 | \mathcal{H} | \hbar_i m_i)(\hbar_i m_i | \mathcal{H} | \hbar_k m_k)(\hbar_k m_k | \mathcal{H} | \hbar_0 m_0)}{(E_{00} - E_{ij})(E_{00} - E_{kl})} - (\hbar_0 m_0 | \mathcal{H} | \hbar_0 m_0) \sum_{k,l}' \frac{(\hbar_0 m_0 | \mathcal{H} | \hbar_k m_k)(\hbar_k m_k | \mathcal{H} | \hbar_0 m_0)}{(E_{00} - E_{kl})^2} \quad (E-5)$$

Using the fact that matrix elements of $\mathcal{H}_{hfs}$ vanish for all but s states of hydrogen, we get for the linear term

$$\Delta E_{hfs} = 2 \sum_i' \sum_{k,l}' \frac{(\hbar_0 m_0 | \mathcal{H}_{hfs} | \hbar_i m_i)(\hbar_i m_i | \mathcal{H}_v | \hbar_k m_k)(\hbar_k m_k | \mathcal{H}_v | \hbar_0 m_0)}{(E_{00} - E_{i0})(E_{00} - E_{kl})} - (\hbar_0 m_0 | \mathcal{H}_{hfs} | \hbar_0 m_0) \sum_{k,l}' \frac{(\hbar_0 m_0 | \mathcal{H}_v | \hbar_k m_k)(\hbar_k m_k | \mathcal{H}_v | \hbar_0 m_0)}{(E_{00} - E_{kl})^2} \quad (E-6)$$

which reduces to

$$\Delta E_{hfs} = -(\hbar_0 m_0 | \mathcal{H}_{hfs} | \hbar_0 m_0) \left(\frac{2}{E_H} + \frac{1}{E_H + E_m} \right) E_{vdw} \quad (E-7)$$

The Van der Waals energy E_{vdw} is then found from empirical constants.

The orthogonalization of the hydrogen atom changes the electronic density at the nucleus of the hydrogen atom. This is taken to be the effect of renormalizing the Schmidt functions and leads to an additional shift in the hyperfine splitting:

(E-8)

$$\Delta_{\text{h.f.s.}} = \frac{8\pi g}{3} \beta_e \left(\frac{\mu_H}{I_H} \right) \underline{I} \cdot \underline{S} |h(\text{H}_{\text{nucleus}})|^2$$

$$\approx \frac{8\pi g}{3} \beta_e \left(\frac{\mu_H}{I_H} \right) \underline{I} \cdot \underline{S} |h_0(\text{H}_{\text{nucleus}})|^2 (1 + S^2)$$

where S^2 is the sum of the overlaps with the one-electron wave functions of the neighbors.

The g-shift is found by considering the term

$$\mathcal{H}_{\text{Hfield}(H)} + \mathcal{H}_{L \cdot S} = \frac{e}{2mc} \underline{H} \cdot \underline{L} + \frac{\hbar^2}{2m^2c^2} r^{-1} \frac{\partial V}{\partial r} \underline{L} \cdot \underline{S}. \quad (\text{E-9})$$

Using second-order perturbation theory and keeping the term linear in $\underline{H} \cdot \underline{S}$ we get from the usual sum rule

$$\Delta g = \frac{\hbar^2}{m^2c^2} \frac{(\langle h | r^{-1} \frac{\partial V}{\partial r} L_z^2 | h \rangle)}{E_h}. \quad (\text{E-10})$$

Here E_h is the average excitation energy for hydrogen. This is evaluated by eliminating the argon spin-orbit splitting constant, λ_α , which arises when h , the orthogonalized hydrogen wave function, is replaced by

$$h = \frac{1}{\sqrt{N!}} (\varphi_{\text{hydrogen}} S_{hA3p\sigma} \varphi_{A3p\sigma}^{\text{A,3p}\sigma}). \quad (\text{E-11})$$

The result is

$$\Delta g = \frac{4}{3 E_h} S_{h, A 3 p \sigma}^2 \lambda_{A 3 p \sigma} (\varphi_{h, 3 p \sigma}^0 | L_z^2 | \varphi_{A, 3 p \sigma}^0) \quad (\text{E-12})$$

where $S_{h, 3 p \sigma}$ is the overlap between the hydrogen ground state, φ^0 , and the outer argon $p \sigma$ state $\varphi_{A, 3 p \sigma}^0$.

REFERENCES

1. For reviews see a) W. Low, "Paramagnetic Resonance in Solids", Solid State Physics Supplement 2, 1960.
b) K. D. Bowers and J. Owen, Reports on Progress in Physics 18, 304 (1955).
2. For reviews see a) D. L. Dexter, "Theory of Optical Properties of Imperfections in Non-Metals", Solid State Physics 6, 1958.
b) C. C. Klick and J. H. Schulman, "Luminescence in Solids", Solid State Physics 5, 1957.
c) D. S. McClure, "Electronic Spectra of Molecules and Ionic Crystals I", Solid State Physics 8, 1959, and
"Electronic Spectra of Molecules and Ionic Crystals II", Solid State Physics 9, 1959.
3. For example see D. E. Milligan, R. M. Hexter, and K. Dressler, J. Chem. Phys. 34, 1009 (1961).
4. See F. Seitz, The Modern Theory of Solids, McGraw-Hill Book Company, Inc., New York, 1940.
5. F. Bloch, Z. Physik 52, 555 (1928).
6. W. Heitler and F. London, Z. Physik 44, 455 (1927).
7. For a review see W. Kohn, "Shallow Impurity States in Silicon and Germanium", Solid State Physics 5, 1957.
8. For example see G. H. Dieke and A. B. F. Duncan, Spectroscopic Properties of Uranium Compounds, McGraw-Hill Book Company, Inc., New York, 1949.
9. C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. 104, 599 (1956).
10. C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. 104, 846 (1946).
11. S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, J. Chem. Phys. 32, 963 (1960).

12. a) J. A. Dweck and P. J. Bray, Bull. Am. Phys. Soc. 6, 113 (1961).
b) J. L. Hall and R. T. Schumacher, Bull. Am. Phys. Soc. 6, 247 (1961).
13. R. Livingston, H. Zeldes and E. H. Taylor, Discussions Faraday Soc. 19, 166 (1955).
14. M. McCarty and G. Robinson, Molecular Physics 2, 415 (1959).
15. F. Adrian, J. Chem. Phys. 32, 972 (1960).
16. P. Fontana, "Shifts in Hyperfine Frequencies Caused by Foreign Gases", reported at The Ann Arbor Conference on Optical Pumping, Ann Arbor, Michigan, 1959.
17. H. Margenau, P. Fontana, and L. Klein, Phys. Rev. 115, 87 (1959).
18. For example see A. Gold, Ph.D. Thesis, University of Rochester, 1960 (unpublished).
19. Cf. F. Adrian, op. cit.
20. B. Bleaney and K. W. H. Stevens, Reports on Progress in Physics 14, 108 (1953);
A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A, 205, 135 (1951).
21. C. P. Slichter, Lectures on Electron Spin Resonance Studies in Color Centers delivered at The International Summer Course on Solid State Physics, Ghent, 1961.
22. R. S. Knox, private communication.
23. P. Kusch, Phys. Rev. 100, 1188 (1955).
24. R. Beringer and M. A. Heald, Phys. Rev. 95, 1474 (1954).
25. F. Seitz, op. cit., p. 470.

26. For example see L. I. Schiff, Quantum Mechanics, McGraw-Hill Book Co., Inc., New York, first ed., 1949, p. 321, and E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge University Press, Cambridge, England, 1935, p. 130.
27. For a derivation see L. D. Landau and E. M. Lifschitz, Quantum Mechanics, Pergamon Press Ltd., London, 1958, p. 486, and E. Segrè, Experimental Nuclear Physics, John Wiley and Sons, Inc., New York, 1953, p. 381.
28. Cf. R. S. Knox, Ph.D. Thesis, University of Rochester, 1958 (unpublished) p. 41.
29. F. Seitz, op. cit., p. 73.
30. J. G. Kirkwood, Physik. Z. 33, 57 (1932).
R. A. Buckingham, Proc. Roy. Soc. (London) A, 160, 113 (1937).
31. C. and M. Cuthbertson, Proc. Roy. Soc. (London) A, 84, 13 (1910).
32. See for example L. Pauling and E. B. Wilson, Jr., Introduction to Quantum Mechanics, McGraw-Hill Book Co., Inc., New York, 1935, p. 185.
33. D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A, 166, 450 (1938).
34. R. S. Knox, Phys. Rev. 115, 1095 (1959).
35. P. Bender, "Comments on Dr. Fontana's Paper" made at The Ann Arbor Conference on Optical Pumping, Ann Arbor, Michigan, 1959.
36. R. Herman and H. Margenau, Phys. Rev. 122, 1204 (1961).
37. H. R. Hassé, Proc. Cambridge Phil. Soc. 26, 542 (1930).
38. H. R. Hassé, Proc. Cambridge Phil. Soc. 27, 66 (1931).
39. W. Marshall and R. Stuart, Phys. Rev. 123, 2048 (1961).

40. Cf. J. E. Lennard-Jones, Proc. Roy. Soc. (London) A, 129, 598 (1930).
41. For a discussion of the connection between perturbation theory and the variational method for this problem, see O. Sinanoglu, J. Chem. Phys. 34, 1237 (1961).
42. J. C. Slater and J. G. Kirkwood, Phys. Rev. 37, 682 (1931).
43. R. A. Buckingham, Proc. Roy. Soc. (London) A, 160, 94, 113 (1937).
44. T. Kojima, J. Phys. Soc. of Japan 12, 908 (1957).
45. H. Margenau, Revs. Modern Phys. 11, 1 (1939).
46. Cf. B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943); B. M. Axilrod, J. Chem. Phys. 19, 719, 724 (1951).
47. For a discussion of correlation energies see O. Sinanoglu, J. Chem. Phys. 33, 1212 (1960); O. Sinanoglu, Phys. Rev. 122, 493 (1961).
48. For example see L. Pauling and E. B. Wilson, Jr., op. cit. p. 184.
49. See, for example, J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, New York, 1954.
50. P. O. Löwdin, Adv. in Phys. 5, 1 (1956).
51. For a discussion of distortion around point defects in face-centered cubic lattices see H. Kanzaki, J. Phys. Chem. Solids 2, 24 (1957).
52. J. E. Lennard-Jones, Physica 4, 941 (1937).
53. E. R. Dobbs and G. O. Jones, Reports on Progress in Physics 20, 516 (1957).
54. M. Kunimune, J. Chem. Phys. 18, 754 (1950) and H. Margenau, Revs. Modern Phys. 11, 1 (1939).
55. P. O. Löwdin, Thesis, Uppsala, Sweden (1948); Arkiv. Mat. Astr. Phys. 35A, 9 and 30 (1948).

56. W. E. Bleick and J. E. Mayer, J. Chem. Phys. 2, 252 (1934).
57. G. Breit and I. I. Rabi, Phys. Rev. 38, 2083 (1931).
58. B. M. Axilrod, op. cit.
59. A. Dalgarno and A. E. Kingston,
Proc. Roy. Soc. (London) 73, 455 (1959);
Proc. Roy. Soc. (London) 78, 607 (1961).
60. R. S. Knox and F. Bassani, Phys. Rev. 124, 652 (1961).
61. O. Schnepp and K. Dressler, J. Chem. Phys. 33, 49 (1960).
62. J. C. Phillips, J. Phys. Chem. Solids 11, 226 (1959)
and M. H. Cohen and V. Heine, Phys. Rev. 122, 1823 (1961).
63. A. Gold, Phys. Rev. 124, 1740 (1961).
64. F. C. Brooks, Phys. Rev. 86, 92 (1952).