$\Gamma(\mathbf{k})$ is known experimentally and hence (A17) can be numerically evaluated for a given $\varkappa$ for different q's using R as a parameter. No doubt formula (A17) is valid for all R, but if we follow the above procedure we no more have an explicit formula for the width. Even formula (A17) does not circumvent the difficulty of not knowing $\Gamma(\varkappa)$ very accurately. To see this we proceed to make some approximations.

$$\overline{W}(\varkappa+\mathbf{q})-W(\varkappa)\approx\frac{R}{2\sqrt{\pi}}\frac{1}{\varkappa}\int_0^\infty k\Gamma(k)dk\ \exp\left[-\frac{R^2}{4}(\varkappa-k)^2\right]\frac{1}{2q}\int_{-q}^{+q}\left\{\exp\left[-\frac{R^2}{4}[x^2+2(\varkappa-k)x]\right]-1\right\}dx. \quad \text{(A18)}$$

Expanding the exponential in the curly brackets and integrating we have

$$\overline{W}(\varkappa+\mathbf{q})-W(\varkappa)\approx\frac{R^3}{2\sqrt{\pi}}\frac{a^2}{\varkappa}\frac{1}{12}\int_0^\infty k\Gamma(k)\ \exp\left[-\frac{R^2}{4}(\varkappa-k)^2\right][\tfrac{1}{2}R^2(\varkappa-k)^2-1]dk, \quad \text{(A19)}$$

where we have retained terms up to order q^2 only. From a scrutiny of the integrand one sees the importance of the weighting factors. It is obvious that if the function $\Gamma(\varkappa)$ is not known accurately in the region of $\varkappa$ values where the function is rising rapidly, we would introduce a large error in the value of the integral. It is also clear that one obtains a large negative value for the integral for that value of $\varkappa$ for which there occurs a peak in $\Gamma(\varkappa)$. Detailed numerical computation would be justified when more accurate experimental data are available.

Theory of the Nuclear Magnetic Resonance Chemical Shift of Xe in Xenon Gas*

FRANK J. ADRIAN

Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland

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A theoretical study is made of the density-proportional paramagnetic shift of the resonant magnetic field observed in nuclear magnetic resonance studies of Xe^{129} in pure xenon gas by Streever and Carr. The theory is based on a computation of the chemical shift in "diatomic molecules" formed by colliding Xe atoms, including the effects of van der Waals and exchange interactions on the wave function of the colliding atoms. The results of this calculation show that only the exchange interactions between the colliding atoms make a significant contribution to the chemical shift. When averaged over the various types of collisions, the following value is obtained for the shift in the resonant field: $\Delta H = -2.85(10)^{-7}H\rho$, where H is the field strength and ρ is the density in amagats. This is in order-of-magnitude agreement with the observed result: $\Delta H = -4.3(10)^{-7}\rho H$.

I. INTRODUCTION

NUCLEAR magnetic resonance studies of Xe^{129} ($I=\frac{1}{2}$) in pure xenon gas at high pressures have yielded two interesting and related results.[1,2] First, the spin-lattice relaxation time, although inversely proportional to the density of the gas as expected,[2] was much too short to be accounted for by the relaxation mechanism of magnetic dipole-dipole interactions between the nuclei of colliding atoms.[1] Secondly, there was a paramagnetic shift of the resonant value of the magnetic field, which was proportional to the density of the gas and to the magnetic field strength.

The relation between these results was established by Torrey,[3] who pointed out that in a diatomic molecule, which may be used as an approximate representation of a pair of colliding Xe atoms, Ramsey's theory of magnetic shielding connects the chemical shift and the nuclear-spin rotational coupling constant.[4] The nuclear-spin rotational coupling is a potential relaxation mechanism because it permits the nuclear spins to exchange angular momentum with the rotational momentum of the colliding atoms. Torrey showed that if one assumed that the observed shift in the resonant field was due to chemical shifts in "diatomic molecules" of colliding Xe atoms, and used the experimental value of the shift together with Ramsey's formula to determine the nuclear-spin rotational coupling constant, then one obtained a computed value for the Xe^{129} relaxation time which was in good agreement with experiment.

Therefore, the sole remaining task in connection with this problem is to compute the chemical shift expected for a pair of colliding Xe atoms as a function of separation, and to see whether such a shift averaged over all

[1] R. L. Streever and H. Y. Carr, Phys. Rev. 121, 20 (1961).
[2] E. R. Hunt and H. Y. Carr, Phys. Rev. 130, 2302 (1963).
[3] H. C. Torrey, Phys. Rev. 130, 2306 (1963).
[4] N. F. Ramsey, Phys. Rev. 78, 699 (1950).

types of collisions is in agreement with the observed result. Such a calculation also tells us which of the interatomic forces experienced by the colliding atoms, that is, attractive van der Waals forces and repulsive exchange forces, makes the greatest contribution to the chemical shift. Actually, such a calculation was carried out some time ago by the author in an attempt to explain the Xe^{129} relaxation by the nuclear-spin rotational coupling mechanism.[5] This calculation considered only the van der Waals part of the interatomic interaction and gave a value for the nuclear-spin rotational coupling constant which was much too small to account for the observed relaxation. A more refined calculation of the contribution of the van der Waals forces to the chemical shift, which will be described in this paper, also gives a negligible result. Recent extension of Hartree-Fock calculations to the very large atoms[6] has provided us with xenon atomic orbitals which are sufficiently accurate to permit an approximate calculation of the contribution of exchange forces to the chemical shift. The result of this calculation is sufficiently close to the experimental result to prove that exchange interactions between colliding Xe atoms provide the chemical shift and spin-lattice relaxation of Xe^{129}.

II. THEORY

Let us consider a pair of xenon atoms with a separation R measured along the z axis, and with the external magnetic field along the x axis. We denote these atoms as A and B, and we compute the magnetic shielding for atom A. It has been shown by Ramsey[4] that if the magnetic field is parallel to the internuclear axis of a diatomic molecule, then all magnetic shielding effects which depend on the interaction of the two atoms vanish. Thus, we calculate the chemical shift for the magnetic field perpendicular to the internuclear axis, and later average over all possible field orientations.

The calculation of magnetic shielding effects can be simplified, and physically reasonable approximations made more readily discernible, by proper choice of the gauge of the vector potential of the magnetic field.[7] Since we are computing the magnetic shielding for nucleus A, the best choice for the vector potential $\mathbf{A}_H$ of the external magnetic field $\mathbf{H}$ is

$$\mathbf{A}_H = \tfrac{1}{2}\mathbf{H} \times \mathbf{r}_a, \qquad (1)$$

where $\mathbf{r}_a$ is the radius vector from nucleus A. The advantage of this choice of gauge is that it puts the orbital Zeeman perturbation in terms of angular momenta measured about this nucleus, with the result that contributions from that part of the electronic wave function

which is spherically symmetric with respect to this nucleus can be eliminated by inspection. For another choice of gauge, the contribution of the spherically symmetric part of the wave function, although still zero in principle, appears as two terms whose exact cancelation may be lost in approximate calculations.

In this two-center calculation, however, use of Eq. (1) complicates the vector potential seen by the electrons of atom B. This is a significant feature of the calculation. It is seen below that this vector potential acting on the electrons of atom B produces orbital polarization of the closed electronic shells of this atom, and that the transmission of this orbital polarization to atom A via the exchange interaction produces the observed chemical shift. Except for interatomic exchange terms, however, this form for the vector potential is an unnecessary complication. In computing matrix elements involving orbitals of one atom only, it is possible to choose the gauge separately for each atom so that the vector potential always has the simple form of Eq. (1). Formally, this is done by using gauge-invariant atomic orbitals.[8] For atom B these orbitals are defined by the equation

$$b_i'(\mathbf{r}_b) = b_i(\mathbf{r}_b) \exp(ie\mathbf{A}_{Hb}\cdot\mathbf{r}_b/\hbar c), \qquad (2)$$

where b_i is the ith atomic orbital of B, b_i' is the corresponding gauge invariant orbital, $\mathbf{r}_b$ is the radius vector from nucleus B, and $\mathbf{A}_{Hb}$ is the vector potential at nucleus B. A similar set of orbitals can be defined for atom A. The advantage of the gauge-invariant orbitals is readily seen if we consider the momentum operator $[\mathbf{p}-(e/c)\mathbf{A}_H]$ for a vector potential defined with respect to an arbitrary origin. Using the relation $\mathbf{p}=-i\hbar\nabla$ and Eq. (1) for $\mathbf{A}_H$, it is readily shown that

$$\langle b_j'|\mathbf{p}-(e/c)\mathbf{A}_H|b_i'\rangle = \langle b_j|\mathbf{p}-(e/2c)\mathbf{H}\times\mathbf{r}_b|b_i\rangle. \qquad (3)$$

This equation shows that use of gauge-invariant orbitals for calculating matrix elements of the momentum operator between orbitals centered on the same atom is equivalent to using ordinary orbitals and choosing the vector potential so that it is zero at the nucleus of this atom.

The disadvantage of the gauge-invariant orbitals appears when exchange and overlap integrals must be considered, because such integrals will contain the field-dependent phase factors present in these orbitals. Since exchange and overlap effects are of paramount importance in this calculation, and since the appearance of field-dependent factors in the overlap and exchange integrals is an undesirable complication, we adopt the following procedure. First, we compute the magnetic shielding considering only the relatively long-range van der Waals interaction between the two Xe atoms, using the gauge-invariant orbital procedure. It is found that the resulting chemical shift is negligible. Then we consider the short-range exchange interactions. For this

[5] F. J. Adrian, thesis, Cornell University, 1955 (unpublished); available from University Microfilms, Inc.

[6] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[7] A good discussion of gauge considerations in magnetic shielding calculations is given by C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), Chap. 4.

[8] F. London, J. Phys. Radium 8, 397 (1937); J. A. Pople, Mol. Phys. 1, 175 (1958).

calculation we choose the gauge so that the vector potential is given by Eq. (1).

A. van der Waals Interaction

Following the procedure just discussed, we use ordinary atomic orbitals, and pick the gauge independently for each atom so that each atomic orbital sees a vector potential of the form of Eq. (1) with the origin at the center of the orbital. This gives the following Hamiltonian:

$$\mathcal{H}=\sum_{\nu}{}^{A} (2m)^{-1}[\mathbf{p}_{\nu}-(e/2c)\mathbf{H}\times\mathbf{r}_{a\nu}-(e/c)\mathbf{A}_{Na\nu}]^2$$
$$+\sum_{\nu}{}^{B} (2m)^{-1}[\mathbf{p}_{\nu}-(e/2c)\mathbf{H}\times\mathbf{r}_{b\nu}-(e/c)\mathbf{A}_{Na\nu}]^2$$
$$+V_A+V_B+\mathcal{H}_V. \quad (4)$$

Here, $\sum_{\nu}{}^{A}$ and $\sum_{\nu}{}^{B}$ denote the sum over the electrons of A and B, respectively; V_A and V_B are the internal potential energies of atoms A and B, and $\mathcal{H}_V$ is the van der Waals interaction Hamiltonian. The quantity $\mathbf{A}_{Na\nu}$ is the vector potential of the magnetic moment of nucleus A acting on the νth electron. It is given by the expression

$$\mathbf{A}_{Na\nu}=\mathbf{\mu}_A\times\mathbf{r}_{a\nu}/r_{a\nu}{}^3, \quad (5)$$

where $\mathbf{\mu}_A$ is the magnetic moment of nucleus A. We neglect all terms associated with the operation of $\mathbf{A}_{Na\nu}$ on electrons of B. It has been shown by Torrey[3] that such terms are negligible, the reason for this being that the magnetic effects associated with the nuclear moment of A fall off rapidly (as $1/r_a{}^3$) with distance. Thus, expanding the Hamiltonian of Eq. (4) and retaining only those terms which contribute to the magnetic shielding gives the effective Hamiltonian

$$\mathcal{H}=\mathcal{H}_A+\mathcal{H}_B+\mathcal{H}_V+\sum_{\nu}{}^{A} (e^2H\mu_A/2mc^2)$$
$$\times(y_{a\nu}{}^2+z_{a\nu}{}^2)/r_{a\nu}{}^3+\sum_{\nu}{}^{A} (\beta H L_{ax\nu}$$
$$+2\beta\mu_A L_{ax\nu}/r_{a\nu}{}^3)+\sum_{\nu}{}^{B} \beta H L_{bx\nu}. \quad (6)$$

In deriving the foregoing Hamiltonian we have also used the facts that the magnetic field $\mathbf{H}$ is directed along the x axis and that the nuclear moment of A is quantized in the direction of $\mathbf{H}$. The new symbols in Eq. (6) have the following meanings: $\mathcal{H}_A$ and $\mathcal{H}_B$ are the Hamiltonians of the isolated atoms A and B, respectively; β is the Bohr magneton; and $L_{ax\nu}$ and $L_{bx\nu}$ denote the x component of the orbital angular momentum of the νth electron about the nuclei A and B, respectively. The orbital angular momenta are in units of $\hbar$.

Let us take the zero-order Hamiltonian to be $\mathcal{H}_A$ $+\mathcal{H}_B+\mathcal{H}_V$, and compute up to second order those terms in the perturbation energy which are linear in H and μ_A. Following Ramsey,[4] we equate the resulting change in the nuclear Zeeman energy to a change $-\sigma_x H$ in the magnetic field at the nucleus, where the magnetic shielding constant σ_x is given by the expression

$$\sigma_x=(e^2/2mc^2)\langle 0|\sum_{\nu}{}^{A} (y_{a\nu}{}^2+z_{a\nu}{}^2)/r_{a\nu}{}^3|0\rangle$$
$$+2\beta^2\sum_{n}{}'(E_0-E_n)^{-1}[\langle 0|\sum_{\nu}{}^{A} L_{ax\nu}/r_{a\nu}{}^3|n\rangle$$
$$\times\langle n|\sum_{\mu}{}^{A}L_{ax\mu}+\sum_{\mu}{}^{B} L_{bx\mu}|0\rangle+CC]. \quad (7)$$

Here, CC denotes the complex conjugate of the first term in the square brackets.

The first term in Eq. (7) is just the diamagnetic shielding of the isolated atom plus small changes due to the perturbation of the Xe atom wave function by the van der Waals interaction. It is readily shown, as it has been by Torrey,[3] that the change in the diamagnetic shielding due to the van der Waals interaction is negligibly small. The reason for this is that the slowly varying function $(1/r)$ is very insensitive to small changes in the wave function.

Thus, we turn to the paramagnetic shielding which is given by the second term in Eq. (7). Here, there is the possibility that the van der Waals perturbation of the atomic wave functions, which may be described as a partial excitation of the $5p$ orbitals to higher states, combined with the Zeeman interaction between the external magnetic field and the orbital momentum of these distorted orbitals, produces a net electronic current in the Xe $5p$ orbitals. Such a current would produce a large magnetic field at the nucleus and, hence, a large magnetic shielding. The results of this calculation show, however, that this effect is small because of almost complete cancelation of terms corresponding to currents of this type.

In this calculation, the problem of summing over a variety of excited states is treated by the usual method of equating the energy of all excited states to an average value. This should be a reasonably good approximation because the energy difference between the lowest excited state of an Xe atom and the ionized atom is small compared to the ionization potential. Since the lower excited states should make a somewhat larger contribution to the sums than the higher states, we take the average energy of an excited state to be given by the formula

$$\Delta E=\langle E_0-E_n\rangle_{av}=\tfrac{2}{3}(E_0-E_1)-\tfrac{1}{3}E_{ion}\cong-9.6\text{ eV}. \quad (8)$$

Here, E_1 is the energy of the lowest excited state and E_{ion} is the ionization energy.[9] By use of this approximation, the paramagnetic part of the magnetic shielding constant, given by the second term in Eq. (7), can be rewritten as

$$\sigma_{px}=(4\beta^2/\Delta E)\langle 0|(\sum_{\nu}{}^{A} L_{ax\nu}/r_{a\nu}{}^3)$$
$$\times(\sum_{\mu}{}^{A} L_{ax\mu}+\sum_{\mu}{}^{B} L_{bx\mu})|0\rangle. \quad (9)$$

The van der Waals Hamiltonian has the form[10]

$$\mathcal{H}_V=(-e^2/R^3)$$
$$\times\sum_{\lambda}{}^{A} \sum_{\eta}{}^{B}(2z_{a\lambda}z_{b\eta}-x_{a\lambda}x_{b\eta}-y_{a\lambda}y_{b\eta}), \quad (10)$$

where the two sets of coordinates with origins at A and

[9] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932), p. 505.

[10] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 923.

B, respectively, are related by the transformations

$$x_b = x_a; \quad y_b = y_a; \quad z_b = z_a + R. \tag{11}$$

The van der Waals perturbed wave function to terms in first order is

$$\Psi = \alpha_0\beta_0 + \sum_{i,j}{}' \frac{\langle \alpha_0\beta_0 | \mathcal{3C}_V | \alpha_i\beta_j \rangle}{(E_0 - E_i) + (E_0 - E_j)} \alpha_i\beta_j, \tag{12}$$

where α_0 and α_i denote, respectively, the ground and ith excited states of the isolated atom A, and similarly for β_0 and β_j. Even though the change in the magnetic shielding is of second order in the van der Waals interaction, we do not need to consider second-order terms in the van der Waals perturbed wave function. This is because all cross products involving the ground-state and second-order terms in the van der Waals perturbed wave function vanish because of the identity

$$(\sum_\mu{}^A L_{ax\mu} + \sum_\mu{}^B L_{bx\mu})\alpha_0\beta_0 = 0. \tag{13}$$

Use of Ψ given by Eq. (12) as the ground-state wave function in Eq. (9) for σ_{px}, and summation over the excited states by use of the "average-energy approximation" for the energy denominators of Ψ, gives the equation

$$\sigma_{px} = [\beta^2/(\Delta E)^3]$$
$$\times \langle \alpha_0\beta_0 | \mathcal{3C}_V (\sum_\nu{}^A L_{ax\nu}/r_{a\nu}{}^3)$$
$$\times (\sum_\mu{}^A L_{ax\mu} + \sum_\mu{}^B L_{bx\mu}) \mathcal{3C}_V | \alpha_0\beta_0 \rangle. \tag{14}$$

The evaluation of this expression is straightforward. In its evaluation two classes of terms arise according to whether the operator $L_{ax\nu}/r_{a\nu}{}^3$ operates on the same electron orbital as the van der Waals operators or on a different orbital. It is the latter class of terms which describes the potentially large effect of the van der Waals excitation of a $5p$ electron followed by a magnetic-field-induced current in the resulting $5p$ "hole." These large terms vanish if one includes intratomic exchange terms, a necessary step which was omitted in the author's original calculation.[5] Thus, it is found that the contribution of the van der Waals interaction to σ_{px} is given by the expression

$$\sigma_{px} = [36e^4\beta^2/R^6(\Delta E)^3] \langle r^2 \rangle_{5p} \langle 1/r \rangle_{5p}, \tag{15}$$

where $\langle r^2 \rangle_{5p}$ and $\langle 1/r \rangle_{5p}$ are the expectation values for a Xe $5p$ orbital. A rough estimate of this quantity shows that it is negligible. Taking $\langle 1/r \rangle_{5p} = 1a_0$, $\Delta E = -9.6$ eV, and introducing the experimental value of the polarizability[11] α through the approximate relation[12] $\alpha = 4e^2 \langle r^2 \rangle_{5p}/\Delta E$, gives $\sigma_{px} = -(10)^{-8}$ at $R = 4$ Å. This is already less than the observed shift at 1 amagat density[1,2] and is completely negligible when one aver-

ages over collisions, since a given atom only spends a very small fraction of its time within 4 Å of another atom.

The perfect cancellation of the large terms in summing Eq. (14) for σ_{px} is, of course, a result of the average energy approximation. Since the dependence of these large terms on the radial integrals is $\langle r^2 \rangle_{5p}{}^2 \langle 1/r^3 \rangle_{5p}$, which is several orders of magnitude larger than $\langle r^2 \rangle_{5p} \langle 1/r \rangle_{5p}$, the following check was made on the accuracy of the "average-energy approximation." The obvious differences in excitation energies depend on whether the $5p$ electron is excited to an s, p, or d orbital, and the spin-orbit energy of the resulting $5p$ "hole." Thus, a calculation was performed in which excited states were classified according to whether the excited electron was in an s, p, or d state and whether the $5p$ "hole" was $5p_{3/2}$ or $5p_{1/2}$, and different excitation energies were assigned to the various types of excited states. (The classification of the various excited states and their separate summation was done with the aid of conventional methods of computing matrix elements of angular momentum operators.[13])

This calculation, which, although fairly straightforward, is too lengthy to describe in detail here, gave the expected result. This was that no reasonable assignment of the various excitation energies gave a result for σ_{px} which was appreciably greater than the result given by Eq. (15).

B. Exchange Interactions

We now consider the contribution of exchange interactions between the colliding atoms to the magnetic shielding. As discussed previously, we take the vector potential in this calculation to be given by Eq. (1). Now it may seem inconsistent to choose one gauge for computing the exchange terms, while using a different approach based on gauge-invariant orbitals for computing those magnetic shielding effects which do not involve interatomic exchange. This, however, is not the case because, in this calculation, we can always distinguish between exchange and nonexchange terms no matter what gauge is used. Consequently, each set of terms will be individually gauge invariant, and each can be computed using the most convenient choice for the vector potential. In fact, this calculation can be carried out using the vector potential of Eq. (1) throughout with the same results. The only difference is that in this approach two large terms of opposite sign appear in the nonexchange part of the magnetic shielding. It can be shown that these terms cancel exactly, but their appearance lengthens the discussion of the previous section, and detracts from its clarity.

With the vector potential of the external field given by Eq. (1), the same procedures that led to the Hamil-

[11] *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 36, p. 192.

[12] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 354.

[13] G. Racah, Phys. Rev. **62**, 438 (1942).

tonian of Eq. (6) give the Hamiltonian

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_{AB} + \sum_{\nu}{}^A (e^2 H \mu_A/2mc^2)$$
$$\times (y_{a\nu}{}^2 + z_{a\nu}{}^2)/r_{a\nu}{}^3 + \sum_{\nu}{}^A (\beta H L_{ax\nu}$$
$$+ 2\beta\mu_A L_{ax\nu}/r_{a\nu}{}^3) + \sum_{\nu}{}^B \beta H L_{ax\nu}. \quad (16)$$

The only differences between this Hamiltonian and that of Eq. (6) are that the interaction between atoms is now represented by $\mathcal{H}_{AB}$, and, as a consequence of our choice of vector potential, all orbital angular momenta are measured with respect to nucleus A.

It is readily shown that the change in the diamagnetic shielding due to the exchange interaction is negligible. Let us take the ground-state wave function to be an antisymmetrized product of one-electron orbitals of the interacting atoms

$$|\alpha_0\beta_0\rangle = \mathcal{Q} a_{x,0}(1) a_{y,0}(2) a_{z,0}(3) b_{x,0}(4) b_{y,0}(5) b_{z,0}(6). \quad (17)$$

Here, $\mathcal{Q}$ denotes the operation of antisymmetrization and renormalization; $a_{x,0}$, $a_{y,0}$, and $a_{z,0}$ are the $5p$ orbitals of atom A directed along the x, y, and z axes, respectively; and $b_{x,0}$, $b_{y,0}$, and $b_{z,0}$ denote the corresponding orbitals for atom B. Since we are neglecting spin-orbit effects, we can treat the set of electrons with spin "up" separately from the set of electrons with spin "down." Thus, the wave function in Eq. (6) and all subsequent calculations include only that set of electrons with one of the two possible spin orientations. The results of these calculations will thus be multiplied by two to obtain the total result. With this wave function, it is readily shown that the change in σ_{dx} due to the exchange interaction is given by the approximate formula

$$\Delta\sigma_{dx} \cong - (e^2/mc^2)\langle a_{z,0} | b_{z,0}\rangle$$
$$\times \langle b_{z,0} | (y_a{}^2 + z_a{}^2)/r_a{}^3 | a_{z,0}\rangle$$
$$\cong - (2e^2/mc^2 R)\langle a_{z,0} | b_{z,0}\rangle^2. \quad (18)$$

Since, as is discussed below, $\langle a_{z,0} | b_{z,0}\rangle^2 = 4.3(10)^{-3}$ at

$R = 4$ Å, $\Delta\sigma_{dx} = -6(10)^{-8}$. This is negligible when averaged over collisions.

Thus, we turn to the effect of exchange interactions on the second-order paramagnetic shielding. If we neglect possible effects due to the distortion of the ground-state wave function by the exchange interaction, the qualitative features of this process are as follows. If the operator $\sum_{\nu}{}^B L_{ax\nu}$ is expanded in terms of coordinates of atom B using the coordinate transformation given by Eq. (11), the result is

$$\sum_{\nu}{}^B L_{ax\nu} = \sum_{\nu}{}^B L_{bx\nu} - iR(\partial/\partial y_{b\nu}). \quad (19)$$

The operator $iR(\partial/\partial y_b)$ can couple excited states of atom B with the ground state, thereby producing orbital polarization of this atom. In the absence of interatomic exchange, atom A is unaware of the orbital polarization of B, and the magnetic shielding at A is unaffected by this polarization. Exchange interactions permit a partial transfer of the polarization of B to A, or, in other words, complete a circuit for the flow of field-induced electron currents from B to A. This current results in an additional magnetic field at nucleus A.

The transfer of the orbital polarization from B to A occurs in two ways. The first way, which we call the overlap effect, is a consequence of the overlap of the orbitals of A and B combined with the Pauli exclusion principle. The second way, which we call excitation transfer, occurs because the exchange interaction couples states such as $|\alpha_0\beta_n\rangle$, where A is in the ground state and B in the nth excited state, with states such as $|\alpha_m\beta_0\rangle$, where A is excited to the mth excited state and B is in the ground state. The exchange coupling of such states is described by the matrix element $\langle \alpha_m\beta_0 | \mathcal{H}_{AB} | \alpha_0\beta_n\rangle$. The exchange interaction can also couple the state $|\alpha_0\beta_n\rangle$ to doubly excited states such as $|\alpha_m\beta_k\rangle$, but we neglect these highly excited states. A perturbation theory calculation of the paramagnetic shielding incorporating these effects gives the following equation for σ_{px}:

$$\sigma_{px} = 2\beta^2 \left[\sum_n{}' \frac{\langle \alpha_0\beta_0 | \sum_{\mu}{}^A L_{a\mu x}/r_{a\mu}{}^3 | \alpha_0\beta_n\rangle \langle \alpha_0\beta_n | \sum_{\nu}{}^B -iR(\partial/\partial y_{b\nu}) | \alpha_0\beta_0\rangle}{E_0 - E_n} \right.$$

$$\left. + \sum_n{}' \sum_m{}' \frac{\langle \alpha_0\beta_0 | \sum_{\mu}{}^A L_{a\mu x}/r_{a\mu}{}^3 | \alpha_m\beta_0\rangle \langle \alpha_m\beta_0 | \mathcal{H}_{AB} | \alpha_0\beta_n\rangle \langle \alpha_0\beta_n | \sum_{\nu}{}^B -iR(\partial/\partial y_{b\nu}) | \alpha_0\beta_0\rangle}{(E_0 - E_m)(E_0 - E_n)} + CC \right]. \quad (20)$$

Here, CC denotes the complex conjugate of the expression in the square brackets. The first sum in the brackets represents the overlap effect, and the second sum is due to the excitation-transfer effect. As usual, the sum over the excited states in Eq. (20) is performed by replacing all the energy denominators by the average excitation energy given in Eq. (8).

There are several different sums in Eq. (20), depending on which orbital of B is initially excited. Let us consider the case where the $b_{z,0}$ orbital in Eq. (17) is excited. It is easily seen that the operator $iR(\partial/\partial y_b)$ can couple this orbital with excited orbitals of d_{yz} symmetry, which are denoted as $b_{yz,n}$. When this excitation is transferred to atom A, the excited states of A must have the corresponding symmetry, namely, they must be antisymmetric with respect to reflection in the xz plane. Such states can result either from the excitation of the $a_{z,0}$ orbital to any excited orbital of y symmetry,

that is,

$$a_{z,0} \rightarrow a_{y,m} \qquad (21)$$

or the excitation of the $a_{y,0}$ orbital to any excited orbital of z symmetry, namely,

$$a_{y,0} \rightarrow a_{z,m}. \qquad (22)$$

For the excitation described by Eq. (21), the matrix element of the exchange interaction which transfers the excitation from B to A is

$$\langle \alpha_m \beta_0 | \mathcal{3C}_{AB} | \alpha_0 \beta_n \rangle$$

$$= - \int a_{z,0}(1) b_{yz,n}(2) \mathcal{3C}_{AB} b_{z,0}(1) a_{y,m}(2) d\tau_1 d\tau_2. \quad (23)$$

Unfortunately, the evaluation of this integral cannot be performed with any degree of precision because of our ignorance of the excited-state wave functions. The best we can do is follow an approximation sometimes used in molecular orbital theory[14] and set this integral equal to the product of the corresponding overlap integrals and an energy factor. This energy factor should be negative, since exchange integrals involving overlapping orbitals are negative and of the order of the excitation energy ΔE. This approximation gives the result

$$\int a_{z,0}(1) b_{yz,n}(2) \mathcal{3C}_{AB} b_{z,0}(1) a_{y,m}(2) d\tau_1 d\tau_2$$

$$= \Delta E \langle a_{z,0} | b_{z,0} \rangle \langle b_{yz,n} | a_{y,m} \rangle. \quad (24)$$

For the excitation described by Eq. (22), the matrix element $\langle \alpha_m \beta_0 | \mathcal{3C}_{AB} | \alpha_0 \beta_n \rangle$ is given by an exchange integral between mutually orthogonal orbitals. Such an exchange integral will be considerably smaller than the exchange integral in Eq. (23) which involves overlapping orbitals. We therefore neglect excitation transfers of the type described by Eq. (22).

Using the approximation given in Eq. (24) for the excitation-transfer integral all of the sums involved in Eq. (20) for σ_{px} can be evaluated. We describe this process in some detail for the initial excitation $b_{z,0} \rightarrow b_{yz,n}$ combined with the excitation transfer state $a_{z,0} \rightarrow a_{y,m}$. In simplifying Eq. (20), we recall that the effect of the operator L_{ax} on p orbitals of A is given by the relations

$$L_{ax} a_x = 0; \quad L_{ax} a_y = i a_z; \quad L_{ax} a_z = -i a_y. \quad (25)$$

We need not consider the effect of L_{ax} on non-p orbitals of A, because the matrix elements of the operator L_{ax}/r_a^3 vanish for all such orbitals. Reduction of Eq. (20) using Eq. (8) and Eqs. (23) to (25) gives the partial

[14] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Company, Inc., New York, 1962), p. 162.

result

$$\sigma_{px}(b_{z,0} \rightarrow b_{yz,n})$$

$$= \left(\frac{4\beta^2 \langle a_{z,0} | b_{z,0} \rangle i}{\Delta E} \right) [\langle r^{-3} \rangle_{5p} \sum_n{}' \langle a_{y,0} | b_{yz,n} \rangle$$

$$\times \langle b_{yz,n} | -iR(\partial/\partial y_b) | b_{z,0} \rangle - \langle r^{-3} \rangle_{5p} \langle a_{y,0} | b_{y,0} \rangle$$

$$\times \sum_n{}' \sum_m{}' \langle b_{y,0} | a_{y,m} \rangle \langle a_{y,m} | b_{yz,n} \rangle$$

$$\times \langle b_{yz,n} | -iR(\partial/\partial y_b) | b_{z,0} \rangle$$

$$- \sum_n{}' \sum_m{}' \langle a_{y,0} | r_a^{-3} | a_{y,m} \rangle \langle a_{y,m} | b_{yz,n} \rangle$$

$$\times \langle b_{yz,n} | -iR(\partial/\partial y_b) | b_{z,0} \rangle]. \quad (26)$$

The primes on the summation signs now mean that we omit from the sums orbitals which are occupied in the ground state. The first sum in this equation is due to the overlap effect and the remaining sums are due to excitation transfer. The first sum is readily evaluated because, except for the omission of terms involving occupied d orbitals of atom B, which are small because the overlap of the orbitals of A with the inner orbitals of B is very small, it is given by the relation

$$\sum_n{}' \langle a_{y,0} | b_{yz,n} \rangle \langle b_{yz,n} | -iR(\partial/\partial y_b) | b_{z,0} \rangle$$

$$\cong \langle a_{y,0} | -iR(\partial/\partial y_b) | b_{z,0} \rangle. \quad (27)$$

This is readily seen by considering the expansion of $a_{y,0}$ in terms of the complete set of orbitals of atom B. Using Eqs. (19) and (25) and the Hermitian property of L_{ax} and L_{bx}, we can readily show that

$$\langle a_{y,0} | -iR(\partial/\partial y_b) | b_{z,0} \rangle$$

$$= i[-\langle a_{z,0} | b_{z,0} \rangle + \langle a_{y,0} | b_{y,0} \rangle]. \quad (28)$$

Using the same procedures, we can show that the second sum in Eq. (26) is negligible. The evaluation of the third sum uses the same basic method, but for this case it is not valid to neglect the $5py$ orbital of A in summing over n because the quantity $\langle a_{y,0} | r_a^{-3} | a_{y,0} \rangle$ is very large. Thus, we get the following result for this sum:

$$\sum_n{}' \sum_m{}' \langle a_{y,0} | r_a^{-3} | a_{y,m} \rangle \langle a_{y,m} | b_{yz,n} \rangle$$

$$\times \langle b_{yz,n} | -iR(\partial/\partial y_b) | b_{z,0} \rangle$$

$$= \langle a_{y,0} | -r_a^{-3} iR(\partial/\partial y_b) | b_{z,0} \rangle$$

$$+ \langle r^{-3} \rangle_{5p} \langle a_{y,0} | iR(\partial/\partial y_b) | b_{z,0} \rangle. \quad (29)$$

The first term on the right-hand side of this equation is negligible because of the factor r_a^{-3}, and the second term may be evaluated using Eq. (28). Thus, the total contribution of the excited states corresponding to the initial excitation $b_{z,0} \rightarrow b_{yz,n}$ to the paramagnetic shielding constant, including a factor of two resulting from an identical sum over the set of electrons with opposite spin, is

$$\sigma_{px}(b_{z,0} \rightarrow b_{yz,n}) = (16\beta^2/\Delta E) \langle r^{-3} \rangle_{5p} S_{\sigma\sigma}(S_{\sigma\sigma} + S_{\pi\pi}). \quad (30)$$

In this equation, we have redefined the overlap integrals as follows:

$$S_{\sigma\sigma} = -\langle a_{z,0} | b_{z,0} \rangle; \quad S_{\pi\pi} = \langle a_{y,0} | b_{y,0} \rangle. \quad (31)$$

The sign change in the definition of $S_{\sigma\sigma}$ is a consequence of the choice of coordinate axes made in Eq. (11) which makes $\langle a_{z,0} | b_{z,0} \rangle$ negative.

Using the same procedures, the contribution to σ_{px} resulting from the excitation of a $5py$ orbital of B was computed. The result of this calculation was

$$\sigma_{px}(b_{y,0} \to b_{yy,n}) = (16\beta^2/\Delta E)$$
$$\times \langle r^{-3} \rangle_{5p} S_{\pi\pi}(S_{\sigma\sigma} + S_{\pi\pi}). \quad (32)$$

The excitation of a $5px$ electron of B does not contribute to σ_{px} because the resulting excited states have x symmetry, i.e., they change sign upon reflection in the yz plane. Application of the operator $L_{ax}/r_a{}^3$ to all such states gives zero. Thus, the net paramagnetic shielding due to exchange interactions between the atoms is

$$\sigma_{px} = (16\beta^2/\Delta E)\langle r^{-3} \rangle_{5p}(S_{\sigma\sigma} + S_{\pi\pi})^2. \quad (33)$$

Equation (8) gives $\Delta E = -9.6$ eV, the result $\langle r^{-3} \rangle_{5p} = 1.203(10)^{26}$ cm^{-3} has been computed by Mayer,[15] and a calculation discussed in the following section gives the result $(S_{\sigma\sigma} + S_{\pi\pi})^2 = 0.061$ at $R = 4$ Å. Inserting these values into Eq. (33) gives $\sigma_{px} = -6.55(10)^{-5}$ at $R = 4$ Å, a result which is much larger than the magnetic shieldings resulting from any of the other effects discussed. The reason why this term is so much larger than the others is the presence of the large quantity $\langle r^{-3} \rangle_{5p}$. This indicates that the external magnetic field, aided by the interatomic exchange interactions, has induced an electronic current in the $5p$ orbitals of atom A. This results in a relatively large additional magnetic field at the nucleus of this atom.

Finally, we consider the case where the magnetic field makes an angle θ with the internuclear axis instead of being perpendicular to it. Since, as shown by Ramsey[4] σ_p vanishes when the field is parallel to the internuclear axis of a linear molecule, σ_p for the general case will be given by the formula

$$\sigma_p = (16\beta^2/\Delta E)\langle r^{-3} \rangle_{5p}(S_{\sigma\sigma} + S_{\pi\pi})^2 \sin^2\theta. \quad (34)$$

III. RESULTS AND DISCUSSION

The net paramagnetic shielding of an Xe nucleus in gaseous xenon as a function of density will be given by an average of Eq. (34) for σ_p over all types of collisions. The average over collisions, which is essentially a time average, may, according to the usual procedures of statistical mechanics, be replaced by an ensemble average. This gives us the following expression

for the paramagnetic shielding constant in Xe gas:

$$\langle \sigma_p \rangle = \rho \int \sigma_p(\mathbf{R}) \exp[-U(R)/kT] d\tau. \quad (35)$$

Here, $U(R)$ is the interaction energy of a pair of Xe atoms, and ρ is the density.

For $U(R)$ we have used the modified Buckingham (6-exp) potential[16]

$$U(R) = \frac{\epsilon}{[1-(6/\alpha)]} \left\{ \frac{6}{\alpha} \exp\left(\alpha \left[1 - \frac{R}{R_m} \right] \right) - \left(\frac{R_m}{R} \right)^6 \right\} \quad R \geq R_{\max} \quad (36)$$

$$U(R) = \infty \quad\quad\quad\quad\quad R < R_{\max}.$$

With the aid of experimental data on second virial coefficients and the crystal properties of xenon, Mason and Rice[17] determined the following values for the parameters of this potential: $R_m = 4.450$ Å, $\epsilon/k = 231.2°$K, and $\alpha = 13.0$. This potential has the advantage that it is more flexible than the Lennard-Jones 6-12 potential,[18] and gives a more realistic exponential variation of the repulsive exchange forces. It has the disadvantage of having a spurious maximum at $R = R_{\max}$, but this really offers no difficulty because $R_{\max}$ is much smaller than any reasonable interatomic distance. For this calculation it is helpful to rewrite this potential in the form

$$U(R) = 4\epsilon' \left\{ \exp\left(-\alpha' \left[\frac{R}{R_0} - 1 \right] \right) - \left(\frac{R_0}{R} \right)^6 \right\} \quad R \geqslant R_{\max}, \quad (37)$$

where $R_0 = 3.930$ Å, $\epsilon'/k = 226.1°$K and $\alpha' = 11.48$. The point R_0 where the attractive and repulsive energies cancel may be regarded as the collision diameter, since the steep rise of the repulsive part of the potential does not permit appreciable interatomic penetration beyond this point.

The overlap integrals which determine the dependence of σ_p on R were computed by fitting[19] four exponential terms of the form $ar^4 e^{-br}$ to the outer lobe of the Xe $5p$ Hartree-Fock orbital given by Herman and Skillman.[6] The computation of the overlap integrals could then be performed using the analytical formulas of Mulliken et al.[20] It was found that for the interval 3.5 Å $\leq R \leq 5$ Å,

[15] D. F. Mayers, as quoted by J. R. Morton and W. E. Falconer, J. Chem. Phys. **39**, 427 (1963).

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[16] Reference 10, p. 180.
[17] E. A. Mason and W. E. Rice, J. Chem. Phys. **22**, 843 (1954).
[18] Reference 10, p. 162.
[19] The process of fitting an analytic form to a tabulated wave function is described by J. C. Slater, Phys. Rev. **42**, 33 (1932).
[20] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. **17**, 1248 (1949).

which accounts for nearly the entire contribution to $\langle\sigma_p\rangle$, the function $(S_{\sigma\sigma}+S_{\pi\pi})^2$ could be fitted very well to the simple exponential function $7.27(10)^{-3}\times\exp\{-9.851[(R/R_0)-1]\}$. With this result and the constants given following Eq. (33), $\sigma_p(\mathbf{R})$ can be written as

$$\sigma_p(\mathbf{R})=-7.82(10)^{-5}\exp\{-9.851[(R/R_0)-1]\}\sin^2\theta.$$

$$(38)$$

Insertion of Eqs. (37) and (38) into Eq. (35) gives the result

$$\langle\sigma_p\rangle=-5.21(10)^{-5}(4\pi\rho R_0^3)I(T^*).\qquad(39)$$

Here

$$I(T^*)=\int_0^\infty\left[\exp\left(-9.851(r-1)\right)\right.$$

$$\left.-\frac{4}{T^*}\{\exp[-11.48(r-1)]-r^{-6}\}\right)\right]r^2dr,\quad(40)$$

where $r=R/R_0$ and $T^*=kT/\epsilon'$. The evaluation of this integral, which, together with the other calculations described in this section, was done on a computer, is of some interest because it gives the dependence of $\langle\sigma_p\rangle$ on temperature. The values of $I(T^*)$ at a number of values of T^* are given in Table I.

At room temperature, $T^*=1.31$ and $I(T^*)$ varies slowly with T^* in this region. Thus, it is expected that the variation of $\langle\sigma_p\rangle$ with temperature will be too small to be observed, which is in agreement with the experimental results.[1,2] By plotting the results in Table I it is found that $I(1.31)=0.267$, and our final result for $\langle\sigma_p\rangle$ is

$$\langle\sigma_p\rangle=-2.85(10)^{-7}\rho.\qquad(41)$$

where the density ρ is in amagats. One amagat is the density of an ideal gas at 273°K and 760 mm Hg pressure. The agreement of this result with the experimental result[1,2]

$$\langle\sigma_p\rangle=-4.3(10)^{-7}\rho\qquad(42)$$

is only fair, but is as close as can be expected from an approximate calculation of this type. Thus we may conclude that exchange interactions between colliding Xe atoms are responsible for the observed chemical shift.

Since Torrey[3] has established the connection between the chemical shift resulting from collisions and the re-

TABLE I. Values of the integral $I(T^*)$ which determines the temperature variation of the chemical shift in gaseous xenon. T^* is the reduced temperature kT/ϵ', where ϵ' is a close approximation to the maximum energy of attraction between two Xe atoms.

T^*	1.0	1.5	2.5	5.0	10.0	25.0
$I(T^*)$	0.299	0.254	0.244	0.277	0.358	0.557

laxation of Xe^{129}, there is no need to repeat this calculation. Moreover, Torrey[3] has pointed out that the relation between the chemical shift and the relaxation time does not depend critically on the way σ_p varies with R. Thus, his result is not appreciably affected by the fact that it is the short-range exchange forces rather than the longer-range van der Waals forces which produce the chemical shift.

Finally, it may be pointed out that a calculation similar to the treatment of the van der Waals forces shows that the chemical shift due to an external electric field acting on an Xe atom is also negligible. Thus, even in collisions of an Xe atom with polar molecules, the chemical shift and relaxation of Xe^{129} are determined solely by the exchange interactions. Thus, measurement of the chemical shift in mixtures of Xe with other gases might shed light on the exchange interaction of Xe with various species, although this method will be limited by the fact that the chemical shift is small and hard to measure except in pure Xe at high pressures. Alternatively, it might be possible to obtain nuclear polarization of Xe^{129} using techniques analogous to those used to obtain polarized He^3.[21] The loss of polarization of such a sample upon introduction of a buffer gas would be a measure of the strength of the exchange interactions between the Xe and buffer gas particles.

ACKNOWLEDGMENTS

[21] G. K. Walters, F. D. Colegrove, and L. D. Schearer, Phys. Rev. Letters 8, 439 (1962).