MO Calculations on Sign and Magnitude of the Metal Spin Density in Alkali Radical Ion Pairs*

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Formulas for the spin density at the metal nucleus in alkali radical ion pairs are derived by means of molecular orbital theory combined with first order perturbation theory. The formulas have been used for computer calculations of the metal spin density in the Na naphthalene (NaNl) ion pair. The results show that the zero- and first-order contributions to the metal spin density are of the same order of magnitude, but have different signs, and that the sign of the total spin density at the Na nucleus varies with the position of the Na ion in the ion pair. The experimentally observed dependence of the sign of the alkali coupling constant upon the atomic number of the metal is related to the difference in polarizing influence exerted by small and large ions on the $\pi$ MO's of the aromatic ion. The temperature dependence of the metal coupling constant is explained by taking into account the change in the average position or the root-mean-square position of the alkali ion with a change in temperature.

I. INTRODUCTION

In 1961, Atherton and Weissman inferred from their ESR experiments on solutions of Na naphthalene (NaNl) that a certain amount of unpaired electron spin density was present at the alkali nucleus in the NaNl ion pair.1 Since then, similar phenomena have been observed for numerous other systems. In 1965, De Boer proposed, on the basis of ESR experiments on Cs pyracene, that this spin density could be positive as well as negative and that sometimes a change in sign could occur with a change in temperature.2 Later a number of systems was found in which a similar change in sign seemed to occur.4 The existence of positive and negative metal spin densities was proven recently by NMR experiments,4-8 and for a few systems a change in sign was indeed observed.4,8 Two trends seemed to emerge from the NMR data. First, the metal hyperfine splitting constant (hfsc) showed a tendency to become negative with increasing atomic number,4,8 a conclusion which was predicted at the same time by others on the basis of ESR data.8 Second, a decrease in temperature was often found to be accompanied by a decrease in the magnitude of the metal hfsc, sometimes resulting in a change in sign from positive to negative.4-8 Several models have been proposed to explain the existence of a nonzero spin density at the metal nucleus and, in a few cases, they have been worked out in detail.

Atherton and Weissman originally suggested that mixing of $\sigma$ orbitals of the metal with $\pi$ orbitals of the aromatic ion might produce metal spin densities of the correct order of magnitude.1 They did not consider the possibility of negative metal spin densities and no detailed calculations were reported. They described the dependence of the metal hfsc on the temperature by considering the vibration the alkali metal presumably performs in the potential well of the ion pair and the dependence of the amplitude of this vibration upon the temperature. Other models, based on earlier theories of Weinstein and Grunwald,10 were proposed to explain the temperature dependence of the metal hfsc: Hirota and Kreilick explained their ESR data by assuming the existence of an equilibrium between solvent separated and contact ion pairs in which the value of the metal hfsc would be different.11 Hogen-Esch and Smid used the same model to explain their uv data.11b On the other hand, NMR data obtained for Cs biphenyl in diglyme could only be explained on the basis of the “static” model of Chang, Slates, and Szwarc.11e Aono and Oohashi performed calculations on NaNl on the basis of a charge transfer model and also calculated the temperature dependence of the Na hfsc, $a$, by using the vibrational model of Atherton and Weissman.12 The slope they calculated for the $a$ vs $T$ curve, however, although of the correct order of magnitude, turned out to be smaller than the experimentally measured slopes. They also indicated that in some systems bonding of the alkali ion with the $\sigma$-electron system of the radical might produce nonzero metal hfsc's. An example of such a system was recently investigated by the NMR method.7 To explain the occurrence of negative metal hfsc, De Boer considered positions of the metal ion in the nodal plane of the first antibonding molecular orbital (MO) of the aromatic $\pi$ system.2 For such a position, the zero order spin density vanishes and first order—possibly negative—contributions become important. He argued that the admixture of metal $\phi$ orbitals into the $\pi$ MO's of the aromatic ion might produce a negative spin density at the metal through core polarization. For the explanation of the temperature dependence of the metal hfsc, he used the vibrational model of Atherton and Weissman.
SPIN DENSITY IN RADICAL ION PAIRS

Pedersen and Griffin performed an INDO calculation for LiNl. They found negative spin densities for short distances between the Li and the Nl ion, but ran into convergence problems for larger distances. The dependence of the Li hfscc on the position of the Li ion in the ion pair seemed to be consistent with an explanation of the temperature dependence of the metal hfscc on the basis of the vibrational model.

The most elaborate calculations up till now were reported by Goldberg and Bolton for different alkali Nl systems. They performed a Hückel–McClelland MO calculation, accounting for the polarization of the p MO’s by the metal ion, and they considered the admixture of the metal valence s orbital into the first antibonding MO of the Nl. However, since they performed only a zero order calculation, they were unable to account for negative spin densities.

In this article we consider ion pairs in which the radical anion is a planar σ system. The case that the alkali ion is bonded to the σ-electron system of the radical is not considered since the mechanism which produces spin density at the metal nucleus in this situation seems to be well understood. General formulas for the metal spin density will be presented in Sec. II. They are derived by means of MO theory and first-order perturbation theory. It is shown that De Boer's original explanation for the occurrence of negative metal spin densities is not valid. The formulas are applied to the special case of a NaNl ion pair and the expressions for the Na hfscc which were used for the computer calculations are given. Details about the calculations and the approximations used are presented in Sec. III and the results are presented and discussed in Sec. IV. On the basis of these results, the dependence of the sign of the metal hfscc upon the atomic number and sign of the hfscc upon temperature are discussed. Finally, a few conclusions are presented in Sec. V.

II. THEORY

For the description of the wave function of the ion pair, we use as MO's linear combinations of carbon 2pσ atomic orbitals (AO's), |x_i>, denoted by Latin subscripts and AO's of the alkali metal, |x_M>, denoted by Greek subscripts. The AO, x_i, is centered on the carbon atom C_i of the aromatic molecule. We assume that the MO’s have been obtained from a variational calculation with a one electron Hamiltonian 3E, so that they are orthogonal and that, as the interaction between metal ion and aromatic ion will usually be small, the MO's, apart from a normalization constant, may be presented by

$$\Phi_i = \Phi_i^0 + \sum_j c_{ij} x_j,$$  \hspace{1cm} (1a)

$$\Phi_M = x_M + \sum_j c_{Mj} \Phi_j^0.$$  \hspace{1cm} (1b)

Here $\Phi_i^0$ represents a π MO of the free aromatic ion, and the $c_{ij}$ and $c_{Mj}$ are mixing constants. The MO's of the ion pair thus closely resemble those of the free ions. The MO's, |Φ_i> and |Φ_M>, will be called "aromatic" and "metallic" MO's, respectively. In substituting the MO's, the following conventions are used. The metal-bonding MO's of the aromatic ion are denoted by $\Phi_i^0$, $\Phi_{M1}$, and the first antibonding MO by $\Phi_{M2}$. The core AO's of the metal are denoted by $X_{M1}$, $X_{M2}$, and the valence AO's by $X_M$, $X_M^\pi$, etc. An arbitrary MO, either metallic or aromatic, which is doubly occupied in the zero-order ground state of the ion pair will be denoted by $\Phi$ and an arbitrary empty MO by $\Phi^\prime$. The zero order ground state wavefunction of the ion pair, corresponding to the configuration Ar~Me+, in which Ar and Me denote, respectively, the aromatic molecule and the metal atom, can now be presented by the Slater determinant

$$\Psi_0 = \left[ \prod_i (1/(N_i^{1/2}) \right] [ \Phi_1 \Phi_2 \cdots \Phi_M \Phi_{M1} \Phi_{M2} \cdots \Phi_j \Phi^\prime ],$$  \hspace{1cm} (2)

in which N is the number of electrons described by the wavefunction. An MO without a bar describes an electron with an α spin and an MO with a bar an electron with a β spin. Taking into account electron correlation results in an improved ground state wavefunction which, apart from a normalization constant, is given by

$$\Psi_i = \Psi_0 + \sum_i \lambda_i \Psi_i,$$  \hspace{1cm} (3)

The summation over i runs over all the excited doublet wavefunctions $\Psi_i$, which are linear combinations of Slater determinants. The mixing coefficients $\lambda_i$ can be calculated by perturbation theory with the use of the perturbation Hamiltonian $3\zeta_i$, defined by

$$3\zeta_i = \sum_{j \neq i} (\Delta^2/r_{ij}).$$

Here $r_{ij}$ is the distance between electrons i and j, e is the electric charge of an electron and the summation is over all pairs of electrons. The spin density $\rho(\mathbf{r})$ at the metal nucleus is given by the expectation value of the spin density operator $\rho_{op}(\mathbf{r})$, in which $\mathbf{r}$ is the radius vector of the metal nucleus. $\rho_{op}(\mathbf{r})$ is defined by

$$\rho_{op}(\mathbf{r}) = M_{\mathbf{z}^{-1}} \sum_i S_{z,i} \delta(\mathbf{r} - \mathbf{r}_i),$$  \hspace{1cm} (4)

in which $S_{z,i}$ is the operator for the z component of the angular momentum of electron i, $M_{\mathbf{z}} = \langle \sum_i S_{z,i} \rangle$, $\delta(\mathbf{r})$ is the Dirac delta function and $\mathbf{r}_i$ is the radius vector of electron i. The summations over i run over all the electron in the wavefunction. Using the Eqs. (3) and
the expression for \(\rho(\mathbf{r}_N)\) becomes

\[
\rho(\mathbf{r}_N) = \langle \Psi_0 | \rho_{\text{op}}(\mathbf{r}_N) | \Psi_0 \rangle + 2 \sum_i \lambda_i | \langle \Psi_0 | \rho_{\text{op}}(\mathbf{r}_N) | \Psi_i \rangle | + \sum_j \sum_k \lambda_j \lambda_k | \langle \Psi_i | \rho_{\text{op}}(\mathbf{r}_N) | \Psi_j \rangle |. \tag{5}
\]

A wavefunction can be characterized by the number of singly occupied MO's in the Slater determinants of which it is built. A wavefunction \(| n \rangle\) of type \(n\) will have \(2n+1\) singly occupied MO's in its Slater determinants; \(\Psi_0\) will be represented by \(|0\rangle\), and the other wavefunctions of type 0 by \(|0'\rangle\). Since \(\rho_{\text{op}}(\mathbf{r})\) is a sum of one electron operators, \(|n | \rho_{\text{op}}(\mathbf{r}) | m\rangle = 0\) unless \(n - m = -1, 0\) or 1. Therefore, if in Eq. (5) the terms quadratic in the \(\lambda\)'s are neglected, only terms like \(|0 | \rho_{\text{op}}(\mathbf{r}_N) | 0'\rangle\), \(|0 | \rho_{\text{op}}(\mathbf{r}_N) | 0'\rangle\), and \(|0 | \rho_{\text{op}}(\mathbf{r}_N) | 1\rangle\) remain. They are discussed below:

1. From the Eqs. (2) and (4), one finds for the first term of Eq. (5)

\[
|0 | \rho_{\text{op}}(\mathbf{r}_N) | 0\rangle = |\Phi_{m+1}(\mathbf{r}_N)\rangle \neq 0. \tag{6b}
\]

2. Since \(\rho_{\text{op}}(\mathbf{r})\) is a sum of one electron operators, it follows that \(|0 | \rho_{\text{op}}(\mathbf{r}_N) | 0'\rangle= 0\) unless the Slater determinants representing \(|0\rangle\) and \(|0'\rangle\) differ in only one MO. Therefore, we only need to consider wavefunctions \(|0'\rangle\) which can be obtained from \(\Psi_0\) by exciting an electron from a doubly occupied MO \(\Phi_0\) into \(\Phi_{m+1}\) or by exciting the unpaired electron out of \(\Phi_{m+1}\) into an empty MO \(\Phi_v\). The wavefunctions belonging to the corresponding excited states will be denoted by \(\Psi_{z,m+1}\) and \(\Psi_{m+1,v}\), respectively, and the corresponding \(\lambda\)'s by \(\lambda_{x,m+1}\) and \(\lambda_{m+1,v}\). The sum of the contributions from these excitations to \(\rho(\mathbf{r}_N)\) together with the term \(|0 | \rho_{\text{op}}(\mathbf{r}_N) | 0\rangle\) discussed above will be denoted by \(\rho_0\). \(\rho_0\) is approximately given by

\[
\rho_0 \approx |\Phi_{m+1}(\mathbf{r}_N)\rangle + \sum_x \lambda_{x,m+1} |\Phi_x(\mathbf{r}_N)\rangle + \sum_y \lambda_{m+1,v} |\Phi_y(\mathbf{r}_N)\rangle + \sum_{xy} \lambda_{x,m+1} \lambda_{m+1,v} |\Phi_x(\mathbf{r}_N)\rangle |\Phi_y(\mathbf{r}_N)\rangle |^2. \tag{6a}
\]

\(\Psi_{z,y} = (6)^{-1/2} [2/(\langle N' \rangle)^{1/2}] \cdots \Phi_{x,N} \cdots \Phi_{z,m+1} \Phi_{z,y} \cdots \Phi_{x,N} \cdots |(N')^{-1/2} | \cdots \Phi_{x,N} \cdots \Phi_{z,m+1} \Phi_{z,y} \cdots \Phi_{x,N} \cdots |. \tag{9}
\]

The corresponding mixing coefficient in Eq. (3) is denoted by \(\lambda_{z,y}\) and, according to first order perturbation theory, is given by

\[
\lambda_{z,y} = \frac{1}{2} (6)^{1/2} [\langle m + 1 | x | m + 1 \rangle/(E_y - E_x)]. \tag{10}
\]

The corresponding contribution to the spin density, which will be denoted by \(\rho_{x,y}\), is given by

\[
\rho_{x,y} = [4/(6)^{1/2}] \lambda_{x,y} | \Phi_x(\mathbf{r}_N) \Phi_y(\mathbf{r}_N) \rangle |, \tag{11}
\]

and the sum of these contributions is denoted by \(\rho_{x}\) and can be presented by the following expression

\[
\rho_{x} = \sum_x \sum_y \rho_{x,y} = [4/(6)^{1/2}] \sum_x \sum_y \lambda_{x,y} | \Phi_x(\mathbf{r}_N) \Phi_y(\mathbf{r}_N) \rangle |. \tag{12}
\]

Here, the summations over \(x\) and \(y\) run over the doubly occupied and the empty MO's of the ion pair in the ground state, respectively. The calculation of \(\rho_{x}\) can be simplified by considering the elements \(\rho_{x,y}\) in more detail. Starting points for the following discussion are the Eqs. (10) and (12).

In the beginning of this section, the MO's were divided into aromatic and metallic MO's. Consequently, the \(\rho_{x,y}\) can be divided into four categories.

A. Local Metal Excitations

The first category derives from excitations \(x \rightarrow y\) in which \(\Phi_x\) and \(\Phi_y\) are a doubly occupied metallic MO \(\Phi_x\) and an empty metallic MO \(\Phi_y\), respectively. They correspond to configurations \(\text{Ar}^- (\text{Me}^{+})^*\) in which the metal ion is in an excited state. The contribution of these excitations to \(\rho_{x}\) is denoted by \(\rho_{M}\) and, according
to take core polarization terms of this type into account in a semiempirical way by adjusting the parameter used in the conversion of spin densities into coupling constants. This will be discussed in Sec. III.

Terms of the type occurring in the second sum of Eq. (13) were originally held responsible for the occurrence of negative spin densities. As mentioned in the Introduction, this assumption is not granted by a more detailed analysis. This can be seen as follows. The second sum in Eq. (13) can be compared with the spin density at the metal nucleus \( \rho(\text{n}^2\text{P}) \) when the free atom is in the \( \text{n}^2\text{P} \) state. \( \rho(\text{n}^2\text{P}) \) can be calculated from the hfsc in the \( \text{n}^2\text{P} \) state, \( A(\text{n}^2\text{P}) \), from the expression

\[
A(\text{n}^2\text{P}) = \frac{3}{2} \pi \gamma_\text{a} \gamma_\text{N} \hbar^2 \rho(\text{n}^2\text{P}),
\]

in which \( \gamma_\text{a} \) and \( \gamma_\text{N} \) denote the gyromagnetic constants of the electron and the alkali nucleus, respectively, \( \hbar \) is the constant of Planck divided by \( 2\pi \) and \( A(n^2P) \) is given in energy units. Values of \( A(n^2P) \) can be obtained from spectroscopic data as explained in the Appendix. Together with values of \( A(n^2S) \), the hfsc in the \( n^2S \) state of the free alkali atom, they are presented in Table I for different alkali isotopes. The data in this table show that, apart from Li, the absolute value of the spin density at the metal nucleus due to core polarization by an \( n \) electron is less than 1% of the spin density brought about by an \( ns \) electron. Moreover, the sign of this contribution changes from negative for Li to positive for Rb and Cs, which is contrary to the trends observed experimentally for the ion pairs as was stated in the Introduction. The second sum in Eq. (13) will therefore be neglected. In conclusion, one can say that \( \rho_M \) will be positive and that its contribution to the total spin density can be accounted for semiempirically. For this reason \( \rho_M \) has been omitted from the final expression for \( \rho_1 \).

**B. Local Aromatic Excitations**

The second category of contributions to \( \rho_1 \) derives from so-called local aromatic excitations, \( \pi \rightarrow \pi^* \), in which both \( x \) and \( y \) denote aromatic MO's. They are the complement of the local metal excitations discussed in the preceding paragraph and correspond to configurations \((\text{Ar}^-)^*\text{Me}^+\) in which the aromatic ion is in an excited state. The sum of the contributions of this type will be denoted by \( \rho_{\text{Ar}} \) and, according to the

| Table I. Isotropic hyperfine splitting constants for the free alkal atoms in the \( n^2S \) and \( n^2P \) state. |
| --- | --- | --- | --- | --- | --- | --- | --- |
| \( ^6\text{Li} \) | \( ^7\text{Li} \) | \( ^23\text{Na} \) | \( ^39\text{K} \) | \( ^85\text{Rb} \) | \( ^87\text{Rb} \) | \( ^133\text{Cs} \) |
| \( A(\text{n}^2\text{S}) \times \hbar^{-3} \), Mc/sec | 152.1 | 401.8 | 886 | 231 | 1012 | 3417 | 2298 |
| \( A(\text{n}^2\text{P}) \times \hbar^{-3} \), Mc/sec | -10.9 | -28.7 | -0.5 | -0.2 | 2 | 8 | 28 |

\( ^a \) Apart from Cs no relativistic or volume corrections have been applied to calculate \( A(n^2\text{P}) \).

\( ^b \) The sign of \( A(n^2\text{S}) \) is uncertain; see the Appendix.

\( ^c \) The integrals \( \langle pq \mid rs \rangle \) which occur in this expression are defined by

\[
\langle pq \mid rs \rangle = \int x_\text{a}^*(1) x_\text{a}^*(2) e^{i/\hbar n} x_\text{a}(1) x_\text{a}(2) dx_1 dx_2.
\]

The first and the second sum in Eq. (13) represent the contributions to the metal spin density from the polarization of the metal core by the unpaired electron through the admixture of \( x_\text{ns} \) and \( x_\text{np} \), respectively, in \( \Phi_\text{np}+1 \).

The first sum in Eq. (13) can be compared with the spin density that can be calculated from the hfsc in the \( n^2P \) state of the free alkali atom, they are presented in Table I for different alkali isotopes. The data in this table show that, apart from Li, the absolute value of the spin density at the metal nucleus due to core polarization by an \( n \) electron is less than 1% of the spin density brought about by an \( ns \) electron. Moreover, the sign of this contribution changes from negative for Li to positive for Rb and Cs, which is contrary to the trends observed experimentally for the ion pairs as was stated in the Introduction. The second sum in Eq. (13) will therefore be neglected. In conclusion, one can say that \( \rho_M \) will be positive and that its contribution to the total spin density can be accounted for semiempirically. For this reason \( \rho_M \) has been omitted from the final expression for \( \rho_1 \).

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Terms of the type occurring in the second sum of Eq. (13) were originally held responsible for the occurrence of negative spin densities. As mentioned in the Introduction, this assumption is not granted by a more detailed analysis. This can be seen as follows. The second sum in Eq. (13) can be compared with the spin density at the metal nucleus \( \rho(n^2P) \) when the free atom is in the \( n^2P \) state. \( \rho(n^2P) \) can be calculated from the hfsc in the \( n^2P \) state, \( A(n^2P) \), from the expression

\[
A(n^2P) = \frac{3}{2} \pi \gamma_a \gamma_N \hbar^2 \rho(n^2P),
\]
Eqs. (10) and (12), is given by
\[
\rho_{\text{Ar}} = \sum_{i} \sum_{j} \rho_{ij} = 2 \sum_{i} \sum_{j} \left\{ \left[ m+1 \right] \left[ j \right] \left| j \right. \left. m+1 \right| \right\} \times \left| \Phi_{i}(\mathbf{r}_{\text{Ar}}) \right| \left| \Phi_{j}(\mathbf{r}_{\text{Me}}) \right|,
\]
(15)
The sumations over \( i \) and \( j \) run over the doubly occupied and the empty MO's, respectively, of the ion pair in the ground state. Unless the admixture of \( s \) orbitals of the metal in the aromatic MO's is large, one expects \( \rho_{\text{Ar}} \) to be small. However, detailed calculations are needed to evaluate sign and magnitude of \( \rho_{\text{Ar}} \).

Results of these calculations are reported in Sec. IV.

The two remaining categories of excitations are so-called "cross excitations," by which an electron is excited out of an aromatic into a metallic MO or vice versa. They correspond to charge transfer (CT) states, and take into account the cross correlation between electrons in different moieties of the ion pair.

C. Aromatic-Metal Cross Excitations

Excitations of an electron out of a doubly occupied aromatic MO \( \Phi_{\text{Ar}} \) into an empty metallic MO \( \Phi_{\text{Me}} \) produce CT states \( \text{Ar}^{*}\text{Me} \) or \( \text{Ar}^{*}\text{Me}^{*} \) in which the aromatic molecule or the aromatic molecule as well as the metal atom is in an excited state. Their total contribution to \( p_{\text{Ar},\text{M}} \) will be denoted by \( \rho_{\text{Ar},\text{M}} \). According to the Eqs. (10) and (12), \( \rho_{\text{Ar},\text{M}} \) is given by
\[
\rho_{\text{Ar},\text{M}} = \sum_{i} \sum_{\mu} \rho_{i,\mu} = 2 \sum_{i} \sum_{\mu} \left\{ \left[ m+1 \right] \left[ i \right] \left| i \right. \left. m+1 \right| \right\} \times \left| \Phi_{i}(\mathbf{r}_{\text{Ar}}) \Phi_{\mu}(\mathbf{r}_{\text{Me}}) \right|,
\]
(16)
in which the summations over \( i \) and \( \mu \) run over the doubly occupied aromatic MO's and the empty metallic MO's, respectively, of the ion pair in the ground state. Since the spin density at the metal nucleus in a CT state like \( \text{Ar}^{*}\text{Me} \) is large, one expects excitations of this type to provide for a substantial contribution to \( \rho_{1} \). The sign of \( \rho_{\text{Ar},\text{M}} \) can possibly be inferred from a consideration of the contribution to \( \rho_{\text{Ar},\text{M}} \) from a particular excitation \( i \rightarrow ns \). From the Eqs. (1) and (16), it follows that an important term in the expression for this contribution \( \rho_{i,ns} \) will be the term
\[
2 \sum_{i} \left\{ \left[ m+1 \right] \left[ i \right] \left| i \right. \left. m+1 \right| \right\} \left| c_{\text{Ar},\mu} \Phi_{i,\mu} \right| \left| \chi_{ns}(\mathbf{r}_{\text{Ar}}) \right|^{2}.
\]
Since the integral will be positive, as will \( E_{\text{Ar}} - E_{\mu} \), and since \( c_{\text{Ar},\mu} \) and \( c_{\text{Ar},\mu}^{*} \) will have different signs, this term will be negative. One expects, therefore, \( \rho_{\text{Ar},\text{M}} \) usually to be negative. Results of calculations on \( \rho_{\text{Ar},\text{M}} \) are reported in Sec. IV.

D. Metal-Aromatic Cross Excitations

Excited configurations which are obtained from the zero-order ground state configuration by exciting an electron from a doubly occupied metallic MO \( \Phi_{\text{Me}} \) into an empty aromatic MO \( \Phi_{\text{Ar}} \) correspond to CT states \( \left( \text{Ar}^{+}\right)^{*}\text{Me}^{+} \) and \( \left( \text{Ar}^{+}\right)^{*}\text{Me}^{+} \), in which the aromatic ion or the aromatic ion as well as the metal ion is in an excited state. Since the metallic MO's \( \Phi_{\text{Me}} \) are core type MO's, which are strongly contracted, the overlap between the metal AO \( \chi_{\text{Me}} \) and the pure aromatic MO \( \Phi_{\text{Ar}}^{0} \) will be small and consequently, their mixing will be small. In addition, \( \lambda_{i,j} \) will be small due to the large difference between \( E_{\lambda} \) and \( E_{\text{Me}} \) (e.g., the first ionization potential of Na amounts to 5.14 eV while the second ionization potential amounts to 47.3 eV)\(^{19} \). On the other hand, the contraction of core \( s \) orbitals will provide for a large probability amplitude of \( \chi_{\text{Ar}} \) at the nucleus. The latter two effects (large energy difference and large density of core \( s \) AO's at the nucleus) also play a role in the local metal excitations discussed above. The overlap effect, however, does not play a role in the local metal excitations, but it does affect the elements \( \rho_{i,j} \), making their total contribution probably smaller than \( \rho_{\text{Ar}} \). Therefore, the effect of metal-aromatic cross excitations on the spin density has been neglected.

The results of the preceding discussion can be summarized and simplified as follows:

(a) The total spin density at the metal nucleus, \( \rho(\mathbf{r}_{\text{Me}}) \), is given by
\[
\rho(\mathbf{r}_{\text{Me}}) = \rho_{0} + \rho_{1}.
\]
(17)
The zero order spin density, \( \rho_{0} \), is \( \geq 0 \) and is given by the Eqs. (6) and (7). The first-order spin density, \( \rho_{1} \), is given by
\[
\rho_{1} = \rho_{\text{Ar}} + \rho_{\text{Ar},\text{M}}
\]
(18)
in which \( \rho_{\text{Ar}} \) and \( \rho_{\text{Ar},\text{M}} \) are given by the Eqs. (15) and (16), respectively.

(b) Of the complete set of AO's of the metal only the valence AO's and higher AO's need to be considered. Since only \( s \) orbitals have a nonzero probability density at the nucleus and since, of these \( s \) AO's, the valence AO will show the largest mixing with the MO's \( \Phi_{\text{Ar}}^{0} \), only this AO will be considered in the calculations. The expressions for the aromatic and metallic MO's then reduce to [cf. the Eqs. (1)]
\[
\Phi_{i} = \Phi_{i}^{0} + c_{\text{Ar},i} \chi_{ns},
\]
(19a)
\[
\Phi_{ns} = \chi_{ns} + \sum_{i} c_{\text{Ar},i} \Phi_{i}^{0}.
\]
(19b)
Finally, for \( \Phi(\mathbf{r}_{\text{Ar}}) \) and \( \Phi_{ns}(\mathbf{r}_{\text{Ar}}) \), the following simplified expressions will be used:
\[
\Phi_{i}(\mathbf{r}_{\text{Ar}}) = c_{\text{Ar},i} \chi_{ns}(\mathbf{r}_{\text{Ar}}),
\]
(20a)
\[
\Phi_{ns}(\mathbf{r}_{\text{Ar}}) = \chi_{ns}(\mathbf{r}_{\text{Ar}}),
\]
(20b)
which means that the terms \( \Phi_{i}^{0}(\mathbf{r}_{\text{Ar}}) \) have been neglected. This is justified because, for instance, for Li, Na, and K, even for a C-Me distance as short as 2 Å, the density of a carbon 2p-\( \text{AO} \) at the metal nucleus is about three orders of magnitude smaller than \( |\chi_{ns}(\mathbf{r}_{\text{Ar}})|^{2} \).

In the next paragraph Eqs. (6), (7), and (15)–(20) will be evaluated for the case of a Na naphthalene (NaNi) ion pair.
E. Application to a NaNl Ion Pair

The molecular axis system used in the calculations on NaNl is shown in Fig. 1. To simplify the discussions and the calculations, we consider only positions of the Na nucleus in the XY plane. This has the advantage that the ion pair has at least Cs symmetry, which allows one to restrict the number of excitations to be taken into account on the basis of symmetry considerations.

The bonding MO's of pure NI are denoted by $x0, \cdots, x10$, the antibonding MO's by $x10, \cdots, x16$. $x10$ is the first antibonding MO. The symmetries of these MO's are given in Table II. The valence s AO of Na will be denoted by $x3s$. In the following, the expressions for $p0$ corresponding parent MO's ($x10$ and $x16$, respectively) do not match; they are therefore neglected. According to Eq. (6), $p0$ becomes

$$P0 = \lambda x3s + \lambda x10 + \lambda x16,$$  \tag{21}

and from the Eqs. (15) and (20), it follows that $p1,s$ is given by

$$p1,s = p1,3s + p1,16 + p1,10,$$  \tag{23}

F. Zero Order Spin Density $p0$

Symmetry arguments show that, apart from the ground state configuration $x10$, the only configurations to be considered for the calculation of $p0$ are given in Table II. The valence s AO of Na will be denoted by $x3s$. In the following, the expressions for $p0$ and $p1$ are given.

G. First-Order Spin Density $p1$

According to Eq. (18), for the calculation of $p1$, only $p1,3s$ and $p1,10$ need to be considered.

1. $p1,3s$

As was done for the calculation of $p0$, one can show from symmetry arguments that the only excitations which may give a substantial contribution to $p1,3s$ are the excitations $1\rightarrow 3s$ and $4\rightarrow 3s$. Thus, according to Eq. (15), $p1,3s$ is given by

$$p1,3s = p1,3s + p4,3s.$$  \tag{25}

III. DETAILS OF THE CALCULATIONS

In the following, the choice of MO's $\Phi_i$, the values chosen for the energies $E_i$ and $E_a$, the formulas and parameters used for the evaluation of $c_{3s,i}$ and $c_{4s,i}$, the calculation of the integrals $\int [ij | kl]$ and $\int [ij | k3s]$, and the value of the parameter used to convert spin densities into coupling constants are discussed. In addition, the evaluation of $p0$ and details about the computer programs are discussed.

A. MO's $\Phi_i$ and Energies $E_i$ and $E_a$

For the MO's $\Phi_i$, Hückel MO's were used.\textsuperscript{20} The energies $E_i$ of the MO's $\Phi_i$ were set equal to the energies of the unperturbed MO's $\Phi_i$. For the energy of the MO $\Phi_1$ a value of $-8.3$ eV was used which is equal to the oxidation potential of neutral NI.\textsuperscript{21} The energies of the other MO's $\phi_i$ were derived from this value by taking the Hückel energy difference between $\Phi_0$ and $\Phi_6$ into account and using for the Hückel resonance integral parameter $\beta$ a value of $-2.371$ eV.\textsuperscript{20,21} The energies $E_i$ are given in Table III. A value for $E_a$ was set by taking the energy difference between $\Phi_0$ and $\Phi_6$ equal to the enthalpy $\Delta H$ of the reaction between atomic Na and NI in solution

$$\text{Na} + \text{NI} \rightarrow \text{Na}^+ \text{NI}^-.$$  \tag{27}

According to this definition, $E_a = E_a = \Delta H$. $\Delta H$ is given by

$$\Delta H = E_{N1} + I_{N1} + \Delta H_{solv} + Q,$$  \tag{27}
in which $E_{N1}$ is the electron affinity of Nl, $I_{Na}$ is the ionization potential of Na, $\Delta H_{solv}$ is the enthalpy change due to the change in solvation of the reactants, and $Q$ is the Coulomb energy of the ions in the ion pair. $\Delta H_{solv}$ depends mainly on the solvation of the Na ion in the ion pair. The quantity $\Delta H'$, defined by

$$\Delta H' = \Delta H + L_{Na},$$

in which $L_{Na}$ is the sublimation energy of metallic Na, has been determined experimentally for a number of systems. Since $L_{Na}=1.013$ eV and $E_{Na}=-5.371$ eV (see Table III), $E_{Na}$ can be calculated directly from the equation

$$E_{Na} = -4.36 - \Delta H' \text{ eV}.\$$

Since $\Delta H'$ varies with solvent, $E_{Na}$ varies with solvent. A minimum of $-4.36$ eV for $E_{Na}$ is found if $\Delta H'=0$. On the other hand, in systems like Na+biphenyl in diethoxyethane (DEE), $\Delta H'$ may become as low as $-0.95$ eV. One expects therefore that for NaNl in different solvents $E_{Na}$ may vary from $-4.4$ eV to $-3.3$ eV. For NaNl in DEE, $\Delta H'=-0.52$ eV, which is probably the reaction enthalpy for the formation of contact ion pairs. Using this value for $\Delta H'$, one finds $E_{Na}=-3.84$ eV. Apart from performing the calculations for $E_{Na}=-3.84$ eV, in the next section the variation of $p_l$ with $E_{Na}$ will be considered. The calculation for $E_{Na}=-3.84$ eV has special significance, since for this value of $E_{Na}$ $\chi_{00}$ and $\Phi_0$ are nearly degenerate, and it becomes of interest to see how $p_l$, $p_{Ar}$, and $p_{Ar,M}$ are affected when appreciable mixing occurs between $\chi_{00}$ and one of the antibonding MO's of Nl.

### B. Coefficients $c_{0s}^i$ and $c_{3s}^i$

For the calculation of the coefficient $c_{0s}^i$, the following formula was used:

$$c_{0s}^i = \frac{\langle \Phi_0^s | \chi_{0s} \rangle}{\langle E_i - E_{Na} \rangle}. \quad (28)$$

and a similar one was used for the calculation of $c_{3s}^i$. $S_{i,0s}$ is the overlap integral between $\Phi_0^s$ and $\chi_{0s}$ and is given by

$$S_{i,0s} = \frac{\langle \Phi_0^s | \chi_{0s} \rangle}{\langle E_i - E_{Na} \rangle}. \quad (29)$$

### C. Integrals $[ij \mid kl]$ and $[ij \mid k \ 3s]$

Integrals $[ij \mid kl]$ were calculated by replacing MO's $\Phi_n$ by $\Phi_0^s$. In this way, the integral $[ij \mid kl]$ becomes a sum of integrals $(pq \mid rz)$. These integrals were evaluated by using the zero differential overlap (ZDO) approximation. Values for the integrals $(pp \mid qq)$ were taken from Table I of Ref. (20).

Integrals $[ij \mid k \ 3s]$ are approximately given by

$$[ij \mid k \ 3s] \approx c_{0s}^i \sum_{l=1}^{10} c_{3s}^l [ij \mid k \ 3s] + \sum_{l=1}^{10} c_{3s}^l [ij \mid k \ 3s]^p, \quad (31)$$

in which the zero superscripts at the integrals indicate that the MO's $\Phi_1 \cdots \Phi_3$ and $\Phi_0$ have been replaced by $\Phi_0^s \cdots \Phi_0^s$ and $\chi_{0s}$, respectively. Evaluation of the second term proceeds as indicated before. In the ZDO approximation the integral $[ij \mid 3s3s]$ is a sum of integrals $(2p_2 \ 2p_2 \mid 3s3s)$ which can be evaluated according to the equation

$$(2p_2 \ 2p_2 \mid 3s3s) = (\pi \pi \mid 3s3s) \sin \theta + (\sigma \sigma \mid 3s3s) \cos \theta. \quad (32)$$

$(\pi \pi \mid 3s3s)$ and $(\sigma \sigma \mid 3s3s)$ are Coulomb repulsion integrals between a Na 3s orbital and a carbon 2p$_z$ and

### Table III. Energies of the aromatic MO’s $\Phi_i$ used in the calculations.

<table>
<thead>
<tr>
<th>MO</th>
<th>$E$, eV</th>
<th>MO</th>
<th>$E$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-12.293</td>
<td>6</td>
<td>-5.371</td>
</tr>
<tr>
<td>2</td>
<td>-10.670</td>
<td>7</td>
<td>-4.465</td>
</tr>
<tr>
<td>3</td>
<td>-9.892</td>
<td>8</td>
<td>-3.746</td>
</tr>
<tr>
<td>4</td>
<td>-9.205</td>
<td>9</td>
<td>-3.001</td>
</tr>
<tr>
<td>5</td>
<td>-8.300</td>
<td>10</td>
<td>-1.378</td>
</tr>
</tbody>
</table>

$H_{i,0s} = (F/2) (E_i + E_{Na}) S_{i,0s}, \quad (29)$

in which $F$ is an adjustable parameter which must satisfy the condition $1 < F < 2$. Usually $F$ is chosen between 1.8 and 2.0. For our calculations, we used for $F$ a value of 2.0. A change in $F$ from 2.0 to 1.9 changed the values of $a_i$ by +0.2 to +0.3 G. Equation (28) is strictly valid only for a variational calculation with a basis set of two orbitals under the condition

$$| \angle \rangle (E_i + E_{Na}) S_{i,0s} | \angle \rangle | E_i - E_{Na} |. \quad (30)$$

Although our basis set consists of 11 orbitals, Eq. (28) is still a good approximation due to the fact that the mixing of the MO's $\Phi_0^s$ with each other under the influence of the Hamiltonian $3C$ is negligible. Condition (30) was always satisfied except for $E_{Na}=-3.84$ eV, in which case $c_{0s}^i$ and $c_{3s}^i$, as calculated from (28), differed by 10%–20% from the values calculated by solving the secular equations for $\Phi_0^s$ and $\chi_{0s}$ exactly. However, this occurred only for a few positions of the Na ion, for which $S_{0s,0s}$ reached a maximum.
2p, orbital, respectively, and \( \theta \) is the angle between the Z axis and the vector connecting the C atom and the Na atom. For large C–Na distances, \( R_0 \) one can use the uniformly charged sphere\(^{27,28} \) or the multipole expansion model\(^{29} \) to evaluate these integrals. For \( R > 4 \, \text{Å} \) these two models give results which differ by less than 1.5%. For small C–Na distances the semiempirical approach of Pariser and Parr\(^{28} \) can be used, according to which the expressions for the integrals become

\[
(\pi \pi \mid 3s3s) = \frac{1}{2} \{(\pi \pi \mid \pi \pi) + (3s3s \mid 3s3s)\} - a_0 R^2 - b_0 R,
\]

\[
(\sigma \sigma \mid 3s3s) = \frac{1}{2} \{(\sigma \sigma \mid \sigma \sigma) + (3s3s \mid 3s3s)\} - a_1 R^2 - b_1 R,
\]

in which \( a_0, b_0, a_1, \) and \( b_1 \) are adjustable constants.

The value of \( (3s3s \mid 3s3s) \) can be calculated from the semiempirical expression\(^{30} \)

\[
(3s3s \mid 3s3s) = I_{Na} - E_{Na}
\]

in which \( E_{Na} \) is the electron affinity of Na. Using values of 5.14 eV and 0 eV for \( I_{Na} \) and \( E_{Na} \), respectively,\(^{19,31} \) one finds

\[
(3s3s \mid 3s3s) = 5.14 \, \text{eV}.
\]

Similarly, one finds\(^ {30} \)

\[
(\sigma \sigma \mid \sigma \sigma) = (\pi \pi \mid \pi \pi) = 10.53 \, \text{eV}.
\]

For the actual calculations the uniformly charged sphere model was used for \( R > 6 \, \text{Å} \). For \( R \leq 6 \, \text{Å} \) the Eqs. (32) were used. The parameters \( a_0, b_0, a_1, \) and \( b_1 \) were determined by calculating \( (\pi \pi \mid 3s3s) \) and \( (\sigma \sigma \mid 3s3s) \) with the uniformly charged sphere model for \( R = 6 \, \text{Å} \) and \( R = 8 \, \text{Å} \) and solving the Eqs. (32) for these parameters. The following values were calculated:

\[
a_0 = 1.34 \, \text{eV/Å}^2, \quad a_1 = 1.37 \, \text{eV/Å}^2, \quad b_0 = -7.4 \times 10^{-2} \, \text{eV/Å}, \quad \text{and} \quad b_1 = -7.7 \times 10^{-2} \, \text{eV/Å}.
\]

D. \( \rho_0 \)

The procedure for the calculation of the coefficients \( c_{a^3} \) and \( c_{a^4} \) outlined above proved to be unsatisfactory for the calculation of \( \rho_0 \) because the coefficient \( \lambda_{a,3} \) occurring in the expression (21) for \( \rho_0 \) became too large by an order of magnitude. This can be seen as follows. In the expression (22b) for \( \lambda_{a,3} \), the sum

\[
\sum_{i=1}^{5} 2[ii \mid 6 \, 3s]
\]

should have a value of about 1 eV in order to provide for a reasonable mixing of the excited state\(^3 \Psi_0 \) with the zero-order ground state \( ^3 \Psi_0 \). This sum is approximately given by

\[
\sum_{i=1}^{5} 2[ii \mid 6 \, 3s] \approx c_{a^3} \sum_{i=1}^{5} 2[ii \mid 6 \, 3s] + c_{a^4} \sum_{i=1}^{5} 2[ii \mid 3s3s].
\]

It appears that the first sum in the right-hand side of this equation amounts to approximately 50 eV while the value of the second sum varies from 25 to 45 eV, depending upon the distance between the Na and the Ni ion. Since it follows from Eq. (28) that \( c_{a^3} \sim c_{a^4} \), \( \lambda_{a,3} \) becomes large leading to a ground state with a considerable amount of CT character, and with a Na hfscc much larger than observed experimentally. One way to avoid this difficulty is to change the ratio of \( c_{a^3} \) and \( c_{a^4} \) by increasing \( c_{a^4} \) until the sums in Eq. (33) cancel. A more complete variational calculation than applied in our case might produce this result. However, theoretical zero order spin densities for the NaNi ion pair have been reported already in the literature by Goldberg and Bolton.\(^ {14} \) We have used these zero-order spin densities rather than changing arbitrarily the constants in the MO \( \Phi_0 \) or \( \Phi_3 \). The values used for \( \rho_0 \) are given in Table IV.

E. Conversion Parameter

For the calculation of the Na hfscc one needs a parameter to convert \( |X_{3a}(r_M)|^2 \) into gauss. The free atom value \( A(3S)/\gamma \Delta = 316.081 \, \text{G} \) (see Table I) could be used, but this value takes into account not only the direct contribution of the 3s electron to the spin density at the metal nucleus, but also the indirect contribution arising from the polarization of the metal core. The free atom value may therefore seem to be too large. However, one can show that the spin density, which in the ion pair is present in \( \Psi_8 \), produces through higher order excitations core polarization in approximately the same proportion as a full electron does in the free atom. An example of this was given by the first sum in Eq. (13). The use of the free atom value, therefore, automatically accounts for the desired amount of core polarization. In our calculations the above given value of \( A(3S)/\gamma \Delta \) was used.

F. Programs

Computations were performed on the Raytheon 706 computer of the Chemistry Department of the University of North Carolina at Chapel Hill. In addition, use was made of the facilities at the UNC computational center.

The formulas for the computation of the overlap integrals \( S_{1,3} \) and the formulas for the calculation of the repulsion integrals were incorporated in subroutines in the main program. The integrals \( [ij \mid kl] \) were calculated with a separate routine.

IV. RESULTS AND DISCUSSION

In this section, the results of the calculations on the metal hfscc, \( \alpha \), in NaNl are presented and discussed. The contributions of various excitations to \( \alpha \) are denoted by the same subscripts as the corresponding spin densities, e.g., \( \alpha_{1,3} \) corresponds to \( \rho_{1,3} \) according to \( \alpha_{1,3} = 316.081 \times \rho_{1,3} \). For \( E_{NaNl} \), a value of \(-3.84 \, \text{eV} \) was used, which is the energy of \( \Phi_3 \) calculated for NaNl in DEE,
as explained in Sec. III. In addition, the variation of the first order contribution to the Na hfsc, \( a_{\text{Na}} \), with a variation of \( E_{\text{d}} \), was investigated. \( E_{\text{d}} \) was allowed to vary between \(-3.30\) and \(-4.40\) eV (see Sec. III).

The spin densities were calculated for the following positions of the Na ion:

(a) Positions above the center of one of the rings of Ni at \( X = 1.21 \text{ Å}, Y = 0.0 \text{ Å}, \) and \( Z = 0.0 \rightarrow 6.0 \text{ Å} \). These positions were chosen to investigate the effect of an increase of the interionic distance on the metal hfsc.

(b) Positions along the \( Z \) axis at \( X = 0.0 \text{ Å}, Y = 0.0 \text{ Å}, \) and \( Z = 0.0 \rightarrow 6.0 \text{ Å} \). These positions are of interest since the zero order spin density vanishes at these positions and the spin density will arise from higher order effects alone.

(c) Positions on an axis parallel to the \( X \) axis at \( X = 0.0 \rightarrow 6.0 \text{ Å}, Y = 0.0 \text{ Å}, \) and \( Z = 3.0 \text{ Å} \). These positions were chosen to investigate the variation of the metal hfsc when the metal moves at constant height above the plane of the Ni ion.

The results are presented in the Figs. 2-4 and in Table V. To show the dependence of the different contributions to \( a_{\text{Na}} \) upon \( E_{\text{d}} \), detailed results are given for the positions mentioned above under (a). For the positions mentioned under (b) and (c), similar variations were found. Although spin densities for positions closer to the anion than 2 Å have probably no physical meaning, they have been included for the sake of completeness.

The Figs. 2(a)–(d) represent values for \( a_{\text{Ar}} \) and \( a_{\text{Ar},\text{M}} \) for positions of the Na ion above the center of one of the rings of Ni, for four different energies \( E_{\text{d}} \). As an example, the contributions to \( a_{\text{Ar}} \) and \( a_{\text{Ar},\text{M}} \) from different excitations are given in Table V for \( Z = 2.5 \text{ Å} \). From the Figs. 2(a)–(d) it appears that \( a_{\text{Ar},\text{M}} \) usually gives by far the largest contribution to \( a_{\text{Na}} \). It was argued in Sec. II that this could be expected, since aromatic-metal excitations produce CT states in which there is a large spin density at the metal nucleus. Moreover, it was argued that \( a_{\text{Ar},\text{M}} \) probably would be negative, which is confirmed by the results presented in the Figs. 2(a)–(d). On the other hand, it appears from the same figures that \( a_{\text{Ar}} \) can be positive as well as negative and that its contribution to \( a_{\text{Na}} \) is small unless \( \chi_{\text{Ar}} \) is strongly admixed with a \( \pi \) MO of the aromatic ion. This occurs in our case for \( E_{\text{d}} = -3.84 \text{ eV} \) and \(-3.65 \text{ eV}, \) which energies are close to the energy of \(-3.748 \text{ eV} \) of the \( \Phi_{\text{Ar}} \). For instance, for \( E_{\text{d}} = -3.84 \text{ eV}, \) the admixture of \( \chi_{\text{Ar}} \) into \( \Phi_{\text{Ar}} \) may become as high as 30\%-40\% for a few positions of the metal ion. When this occurs

Table IV. Zero-order spin densities at the Na nucleus in NaNi for different positions of the cation in the \( XZ \) plane.

Data taken from Ref. (14).

<table>
<thead>
<tr>
<th>( Y = 0.0 \text{ Å}, Z = 0.0 \text{ Å} )</th>
<th>( X = 1.21 \text{ Å}, Y = 0.0 \text{ Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X(\text{Å}) )</td>
<td>( \rho_{\chi}(\times10^3) )</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>0.2</td>
<td>0.18</td>
</tr>
<tr>
<td>0.3</td>
<td>0.43</td>
</tr>
<tr>
<td>0.4</td>
<td>0.77</td>
</tr>
<tr>
<td>0.5</td>
<td>1.13</td>
</tr>
<tr>
<td>0.6</td>
<td>1.52</td>
</tr>
<tr>
<td>0.7</td>
<td>1.90</td>
</tr>
<tr>
<td>0.8</td>
<td>2.30</td>
</tr>
<tr>
<td>0.9</td>
<td>2.75</td>
</tr>
<tr>
<td>1.0</td>
<td>3.25</td>
</tr>
<tr>
<td>1.1</td>
<td>3.76</td>
</tr>
<tr>
<td>1.2</td>
<td>4.25</td>
</tr>
<tr>
<td>1.3</td>
<td>4.70</td>
</tr>
<tr>
<td>1.4</td>
<td>5.05</td>
</tr>
</tbody>
</table>

Table V. Contributions from different excitations to the metal hfsc in NaNi as a function of \( E_{\text{d}} \). The position of the alkali ion in this example is at \( X = 1.21 \text{ Å}, Y = 0.0 \text{ Å}, \) and \( Z = 2.5 \text{ Å}, \) above the center of one of the rings of Ni.

<table>
<thead>
<tr>
<th>( E_{\text{d}} )</th>
<th>( a_{\text{Ar}} )</th>
<th>( a_{\text{Ar}} )</th>
<th>( a_{\text{Ar}} )</th>
<th>( a_{\text{Ar}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-4.40 \text{ eV} )</td>
<td>-0.131</td>
<td>-0.637</td>
<td>0.532</td>
<td>0.095</td>
</tr>
<tr>
<td>(-3.84 \text{ eV} )</td>
<td>0.065</td>
<td>0.302</td>
<td>-0.249</td>
<td>-0.043</td>
</tr>
<tr>
<td>(-3.65 \text{ eV} )</td>
<td>-0.666</td>
<td>-0.355</td>
<td>0.283</td>
<td>0.052</td>
</tr>
<tr>
<td>(-3.30 \text{ eV} )</td>
<td>-0.617</td>
<td>0.130</td>
<td>-1.007</td>
<td>-0.486</td>
</tr>
<tr>
<td>(-3.28 \text{ eV} )</td>
<td>-0.285</td>
<td>-0.183</td>
<td>-0.161</td>
<td>-0.130</td>
</tr>
<tr>
<td>(-3.14 \text{ eV} )</td>
<td>-0.134</td>
<td>-0.346</td>
<td>0.220</td>
<td>0.018</td>
</tr>
<tr>
<td>(-3.0 \text{ eV} )</td>
<td>-1.037</td>
<td>-0.398</td>
<td>-0.948</td>
<td>-0.598</td>
</tr>
<tr>
<td>(-0.0 \text{ eV} )</td>
<td>-1.102</td>
<td>-0.733</td>
<td>-0.665</td>
<td>-0.546</td>
</tr>
</tbody>
</table>
the excitations 1→8 and 4→8 in fact correspond to excited states which have again a large amount of CT character, and it is not surprising that in these cases $\sigma_{\text{Ar}}$ gives a substantial contribution to $a_1$.

In Fig. 3 the values of $a_1$ are presented for the same positions as in the Figs. 2. These data demonstrate that, although the contributions from various excitations to $a_1$ may vary strongly with a variation of $E_{3s}$ (see Table V and Figs. 2), $a_1$ itself varies smoothly with $E_{3s}$. Even strong mixing of $\chi_{3s}$ with an antibonding MO of the aromatic ion does not affect this smooth dependence of $a_1$ upon $E_{3s}$. This may indicate that the different first-order excitations have probably been taken into account in a proper way in the calculations.

Finally, in the Figs. 4(a)-4(c) the values of the total hfsc for the positions mentioned above under (a), (b), and (c) are presented. From these figures it appears that in different regions of space the metal hfsc may have different signs and that, consequently, the sign of the metal hfsc may change with a change in the position of the cation. The data in the Figs. 4(a) and 4(c) show that in the region around the YZ plane, which is an antisymmetry plane of the first antibonding MO of Nl, the metal hfsc is negative. Around this region, $a_0$ is zero or very small and the total hfsc is nearly completely determined by the first-order contribution to the hfsc, $a_1$, which is negative. Figure 4(b) shows that, as the Na ion moves away from the plane of the aromatic ion, the metal hfsc may change sign and become negative before leveling off to zero, apparently because $a_0$ dies away faster with increasing interionic separation than $a_1$. A change in sign also occurs as the alkali ion moves away from the center of the molecule along the $X$ axis as is clear from Fig. 4(c).

The results presented here allow a discussion of the dependence of the sign of the metal hfsc upon the atomic number of the alkali nucleus, $Z_M$, and the dependence of sign and magnitude of the metal hfsc upon the temperature (see the Introduction).

### A. Dependence on $Z_M$

Three parameters may vary systematically with a systematic change in $Z_M$: the energy of the valence $s$ AO of the metal, $E_{3s}$, the position of the alkali ion
spin density, is more likely than for smaller cations on account of Coulomb forces. Theoretical support for this assumption has been reported in the literature.\textsuperscript{12,14} Although this reasoning may be valid for NI, it is difficult to see how similar arguments would apply for any radical ion pair. Nevertheless, the change in sign from positive to negative with increasing $Z_M$ has been observed for instance for ion pairs of naphthalene, anthracene, and biphenyl, and this trend seems to be independent of the anion. The dependence of the sign of the metal hfsc upon the position of the alkali ion can, therefore, probably not provide the explanation for the observed trend.

The third parameter on which the metal coupling constant depends is the overlap of $\chi_{ns}$ with the various MO's of the anion. The value of the overlap integral $S_{i,ns}$ depends on the number of nodes in the MO $\Phi_i$ and upon the polarization of this MO by the alkali ion. As the number of nodes in $\Phi_i$ increases, $S_{i,ns}$ will decrease and so, in general, $S_{i,ns}$ will be smaller for antibonding MO's than for bonding MO's. This is demonstrated by the data in Table VI, which gives the value of $S_{i,ns}$ for different MO's in a NaNl ion pair. On the other hand, electrostatic polarization of the $\pi$ MO's may affect the values of $S_{i,ns}$ appreciably.\textsuperscript{14,18} This effect is characteristic for the alkali ion and is important mainly for the smaller ions like Li$^+$ and Na$^+$. For instance, for NaNl polarization of $\Phi_6$ may increase $S_{6,3s}$ almost by an order of magnitude.\textsuperscript{14} It may also be expected that the overlap of $\chi_{ns}$ with antibonding MO's is more sensitive towards polarization effects than the overlap with bonding MO's: overlap with bonding MO's will usually be large regardless whether or not polarization effects are taken into account. It can be concluded that for small cations $S_{i,ns}$ will be large for both bonding and antibonding MO's $\Phi_i$, while for large cations $S_{i,ns}$ will be large for the bonding MO's, especially the lower ones, and small for the antibonding MO's.

The zero- and first-order contribution to the metal hfsc depend differently on these overlap integrals. $a_0$ depends on the overlap of $\chi_{ns}$ with the first anti-

| Table VI. Values of the overlap integral $S_{i,ns}$ of $\chi_{ns}$ with different Huckel MO's $\Phi_i$ of NI for different positions of the Na ion above the center of one of the rings of NI. No polarization of the MO's was taken into account. |
|---|---|---|---|---|
| X | 2.0 Å | 2.5 Å | 3.0 Å | 3.5 Å | 4.0 Å |
| 1 | $0.206$ | $0.218$ | $0.201$ | $0.168$ | $0.130$ |
| 2 | $-0.064$ | $-0.073$ | $-0.069$ | $-0.057$ | $-0.044$ |
| 3 | $0.022$ | $0.022$ | $0.020$ | $0.017$ | $0.013$ |
| 4 | $-0.002$ | $0.001$ | $0.002$ | $0.001$ | $0.001$ |
| 5 | $-0.011$ | $-0.009$ | $-0.007$ | $-0.006$ | $-0.005$ |
bonding MO, while \( a_1 \) depends by means of the aromatic-metal cross excitations mainly upon the overlap of \( \chi_m \) with the bonding MO’s of the anion. The preceding argument, therefore, shows that with an increase in the size of the cation the contribution of \( a_1 \) to the total hfsc will gain importance over \( a_0 \). Since \( a_1 \) can be expected to be negative, whereas \( a_0 \) is always positive, the total hfsc will show a tendency to become more negative if the size of the alkali ion increases. Further calculations and experiments have to be performed to test this explanation.

B. Dependence Upon the Temperature

It was mentioned in the Introduction that three models have been proposed in the literature to explain the temperature dependence of the metal hfsc in alkali radical ion pairs: the vibrational model of Atherton and Weissman, the equilibrium model of Hirota and Kreilick, and Hogen-Esch and Smid, and the static model of Chang, Slates, and Swarc. Their implications will be discussed briefly in the following on the basis of the results presented in this section.

Aono and Oohashi, using the vibrational model, calculated that from 200 to 300°K the root-mean-square amplitude of the vibration of the Na ion in a NaNl ion pair would increase by approximately 0.2 Å. According to Fig. 4(c), this would correspond with a slope of the \( a \) vs \( T \) curve of about 0.1–0.3 G/100°C. This is of the same order of magnitude as the slope observed for instance for NaNl in tetrahydrofuran (0.4 g/100°C), but it is appreciably lower than the slope observed for instance for NaNl in tetrahydrofuran (THF). Further, the limited experimental evidence available until now seems to indicate that, whenever a change in sign occurs with a change in temperature the change is from positive to negative with decreasing temperature. There is no general way to explain this by invoking the vibrational model, although for the special case of an alkali Ni ion pair the vibrational model could account for such a change in sign, as Fig. 4(c) shows, provided the minimum in the potential energy well of the cation is over the 9–10 bond of Ni.

The equilibrium model explains in a natural way the occurrence of positive and negative slopes in the same \( a \) vs \( T \) curve at different temperatures as was observed for instance for Cs biphenyl ion pairs.

The static model relates the temperature dependence of the metal hfsc to the change in the solvation of the alkali ion with temperature. As the solvation changes, the position of the cation over the plane of the anion as well as the distance to this plane may vary and Figs. 4 show that the sign of the metal hfsc as well as the sign of the slope of the \( a \) vs \( T \) curve may change. Especially towards lower temperatures, as the solvation of the cation increases, the distance between alkali ion and anion will increase which may result in a change in sign of the metal hfsc from positive to negative as Fig. 4(b) shows. This can be related again to the polarizing influence of the cation: as the interionic distance increases, polarization effects will decrease, which causes \( a_0 \) to fall off more rapidly than \( a_1 \). Since the latter can be expected to be negative and \( a_0 \) is always positive, the total coupling constant may show a tendency to become negative at low temperatures.

It can be concluded that, using a combination of the vibrational model and the equilibrium or the static model, one can probably in most cases account for the variation of the metal hfsc with temperature.

Finally, it is remarked that an experimental check of the calculations is not possible as long as the position of the Na ion in the NaNi ion pair has not been established experimentally. The results presented here combined with the observation that the sign of the Na hfsc in NaNl is positive seem to indicate that the position of the Na ion is above one of the rings of the Ni molecule, for which conclusion there is theoretical evidence. Hopefully, experiments on single crystals of alkali radical ion pairs may provide more insight in the structure of these ion pairs.

V. CONCLUSION

The results presented in the preceding section show that the procedure used for the calculation of the first-order spin density gives results of the correct order of magnitude. The difficulties experienced with the calculation of the zero order spin density can possibly be avoided by using an improved variational procedure. The calculations have clearly demonstrated that for an estimate of the total spin density at the metal nucleus, it is not sufficient to calculate the zero order spin density alone: the first-order contribution to the spin density is often of the same order of magnitude and will usually have a different sign. Most important seems to be the conclusion that the metal hfsc may have different signs in different regions of space. Particularly where there is an antisymmetry plane in the first antibonding MO of the aromatic ion, a region of negative spin density will occur. The observation that the metal hfsc has a tendency to become negative with increasing atomic number of the alkali nucleus was related to the
polarizing power of the alkali ions: electrostatic polarization of the π MO's enhances the zero-order spin density compared to the first-order spin density. Thus, going from small, strongly polarizing ions to large, weakly polarizing ions the total spin density will increasingly be determined by the first-order, negative, spin density and thus show a tendency to become negative. This explanation can be checked by performing calculations on Rb-radical ion pairs. The change in weakly polarizing ions the total spin density will in-going from small, strongly polarizing ions to large, polarizing power of the alkali ions: electrostatic power of the alkali ions: electrostatic potential energy well of the alkali ion in the ion pair the distinction between the vibrational and the equilibrium model may become meaningless.

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APPENDIX

In the following, it is shown how the value of the spin density at the nucleus in a free alkali atom can be obtained from spectroscopic data. For the analysis the theory for the hyperfine structure in atomic spectra will be used.

For our purposes we consider the fine structure terms \( n^2S_{1/2} \), \( n^2P_{1/2} \), and \( n^2P_{3/2} \), in which the unpaired electron is present in the valence ns orbital \((n^2S)\) or the valence np orbital \((n^2P)\), respectively. The fine structure levels are split by the hyperfine interaction between the total angular momentum \( J = L + S \) and the magnetic moment of the nucleus, where \( L \) represents the orbital angular momentum and \( S \) the electron spin angular momentum. The energy of each hyperfine level depends only on the total spin \( F \), given by \( F = J + I \), where \( I \) is the nuclear spin angular momentum.

The distance \( W_F \) of the hfs levels, belonging to a particular term, to the center of gravity of this term is given, in energy units, by:

\[
W_F = \frac{(A/2) C + B}{2I(I+1)} \frac{3/2(C+1) - 2I(I+1)J(J+1)}{2I(I+1)2J(J+1)} \quad (A1)
\]

in which \( C = F(F+1) - I(I+1) - J(J+1) \). \( A \) and \( B \) characterize, respectively, the magnetic and the quadrupole interaction between the nucleus and the electrons of the atom (for \( J \leq 1/2 \), \( B = 0 \)).

The magnetic constants pertaining to our problem, are denoted by \( A(n^2S) \), \( a_{1/2} \) and \( a_{3/2} \) for the terms \( n^2S_{1/2} \), \( n^2P_{1/2} \), and \( n^2P_{3/2} \), respectively. Thus, for the energy difference between the two hyperfine levels with \( F = I + 1/2 \) and \( F = I - 1/2 \) of the term \( n^2S_{1/2} \), one finds, using Eq. (A1),

\[
W_{I+1/2} - W_{I-1/2} = \frac{3}{2} A(n^2S) \times (2I+1). \quad (A2)
\]

For the energy differences between the hfs levels of the other terms, similar equations hold. Thus, from a knowledge of the energy differences between the hfs levels, the constants \( A(n^2S) \), \( a_{1/2} \) and \( a_{3/2} \) can be determined.

In general, there are three interactions that contribute to the magnetic constant:

(a) the Fermi contact (Fc) interaction,
(b) the interaction between the nuclear magnetic moment and the orbital momentum of the electrons,
(c) the magnetic point dipole interaction between the nuclear spin and the electron spin.

\( A(n^2S) \) is only determined by the Fc interaction and is given by

\[
A(n^2S) = (8\pi/3)\gamma_z n^2 p(n^2S), \quad (A3)
\]

in which \( p(n^2S) \) is the spin density at the metal nucleus in the \( n^2S \) state of the free atom. Eq. (A3) has a form analogous to that of Eq. (14). \( A(n^2S) \) can be obtained directly from Eq. (A2). Values of \( A(n^2S) \) for different alkali isotopes have been given in Table I.

All three above mentioned interactions contribute to \( a_{1/2} \) and \( a_{3/2} \). The contributions of the Fc interaction are usually denoted by \( a_{c,1/2} \) and \( a_{c,3/2} \), while the sums of the other two contributions are usually denoted by \( a_{d,1/2} \) and \( a_{d,3/2} \). Thus,

\[
a_{1/2} = a_{c,1/2} + a_{d,1/2}, \quad (A4a)
\]

\[
a_{3/2} = a_{c,3/2} + a_{d,3/2}. \quad (A4b)
\]

If volume and relativistic corrections are neglected in the following relations hold between \( a_{c,1/2} \), \( a_{c,3/2} \), \( a_{d,1/2} \), and \( a_{d,3/2} \):  

\[
a_{c,1/2} = -a_{d,1/2}, \quad (A5a)
\]

\[
a_{d,1/2} = 5a_{d,3/2}. \quad (A5b)
\]

Since \( a_{c,3/2} \) is given by \( a_{c,3/2} = (8\pi/9)\gamma_z n^2 p(n^2P) \), one obtains from the Eqs. (14) and (A4)–(A6)

\[
A(n^2P) = \frac{3}{2} (5a_{1/2} - a_{3/2}). \quad (A7)
\]

With the help of this equation, \( A(n^2P) \) can be calculated from the values of \( a_{3/2} \) and \( a_{1/2} \) obtained from op-
tactical double resonance, atomic beam, and level crossing experiments.

The validity of Eq. (A5b) has been questioned in the literature. Lyons et al.\textsuperscript{35} have argued that this equation is strictly valid only for a single particle approach and that the correct value for the constant in this equation is expected to differ from 5. By using Brueckner–Goldstone many-body theory, they showed that for Li the ratio of $a_{3s,1/2}$ and $a_{3s,3/2}$ is equal to 5.35 and that the value of $A(n^2P)$ for Li equals $-28.7$ Mc/sec instead of $-31.6$ Mc/sec, as calculated from Eq. (A7). They indicated a high accuracy for their result (1.5%) which seems to be granted by the success of the many body theory in predicting the hfs constants for Li and other atoms.\textsuperscript{35,36} Svanberg and Rydberg\textsuperscript{37} calculated for Cs a value of 6.95 instead of 5 for the proportionality constant in Eq. (A5b), which changes $A(n^2P)$ for Cs\textsuperscript{33} from $-13$ Mc/sec, as calculated from Eq. (A7), to $+28$ Mc/sec. For Na, K, and Rb, however, Eq. (A7) had to be used since the correct value of the proportionality constant in Eq. (A5b) is not known for these elements. As in the case of Cs, the use of the correct value would probably result in larger values of $A(n^2P)$. The changes, however, can be expected to be not so large as to invalidate the discussion of the local metal excitations given in Sec. II.

The values of $A(n^2P)$ have been given for different alkali isotopes in Table I. For Na and K the sign of $A(n^2P)$, as calculated from Eq. (A7), is of the same order of magnitude as the reported errors in the constants $a_{3s,1/2}$ and $a_{3s,3/2}$.

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