PHYSICAL REVIEW B VOLUME 18, NUMBER 3 1 AUGUST 1978

# Energy and polarizability of atoms in a magnetic field: Donors in silicon

N. O. Lipari
*IBM T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598*

D. L. Dexter
*Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627*

(Received 27 February 1978)

The blinding energy of donors as described by a simple model Hamiltonian in a magnetic field of arbitrary strength is calculated using an expansion of the wave function in terms of spherical harmonics. All the matrix elements are calculated analytically and the Hamiltonian is solved accurately. We then calculate the polarizability by applying a very small electric field. Results are given for P, As, and Sb donors in silicon and are discussed with reference to recent experimental data by Castner and Lee.

## I. INTRODUCTION

Very recently,[1] Castner and Lee have performed static (actually low-frequency) magneto-capacitance measurements at low temperatures in Si with low concentration ($N_D$) of donor impurities, and have interpreted their results as indicating a reduction in the polarizability, $\alpha(H)$, of weakly interacting donors by a static magnetic field.

Theoretically, even though a great deal of work has been done regarding the energy of atoms and donor impurities in the effective-mass approximation (EMA)[2-4] in the presence of a magnetic field, not much exists regarding optical properties, such as dipole-matrix elements, oscillator strengths, etc.[5] In a previous paper,[6] one of us (D.L.D.) has calculated the magnetic-field dependence of the polarizability $\alpha$ for a hydrogenic atom in a weak magnetic field. A simple analytical expression for the ground-state wave function in the presence of a magnetic field was obtained by a variational method. The effect of an electric field, to determine the polarizability, was then calculated using a variational method introduced by Hassé.[7] Analytical expressions for $\alpha_\parallel$ $(\vec{E}\parallel\vec{H})$ and $\alpha_\perp$ $(\vec{E}\perp\vec{H})$ were given. These analytical expressions are however quite complicated, the variational minimization procedure in the presence of the external field is nonlinear, and terms of higher order than $H^2$ were impracticable to consider. In addition, the calculation was performed for hydrogenic atoms only, so that no impurity dependence in $\alpha$ could appear.

The treatment of the energy of donor impurities in multivalley semiconductors is quite complicated,[8-10] and very recently new complications have been pointed out.[11] The inclusion of external fields would make a precise treatment of the problem even more difficult, and is beyond the scope of the present investigation. In this paper we introduce an approximation to describe the spatial dependence of the ground state of the different donors; in view of the crudeness of this approximation the results must be regarded with reservation.

First, we describe a method which provides a good description of the polarizability of the hydrogenic atom for magnetic field of arbitrary strength. Section II describes this method and the solution. In Sec. III we introduce a simple model Hamiltonian for donors. An impurity-dependent potential is introduced and fixed so as to give the measured donor binding energy in the absence of an external field. Finally, in Sec. IV the results for the polarizability are presented and discussed using available experimental data.

## II. HYDROGENIC ATOM: METHOD AND SOLUTION

The EMA leads[2] to the following Schrödinger equation for a hydrogenic impurity in a uniform magnetic field $H_z$, in the $z$ direction:

$$\mathcal{H}_0 = -\nabla^2 - 2/r + \tfrac{1}{4}\gamma^2(x^2+y^2)\,. \tag{1}$$

Here we use the quantities

$$\begin{aligned} a^* &= \epsilon\hbar^2/m^*e^2,\ R^* = m^*e^4/2\epsilon^2\hbar^2\,, \\ \gamma &= \epsilon^2\hbar^3 H_z/m^{*2}e^3c = e\hbar H_z/2m^*cR^*\,, \end{aligned} \tag{2}$$

as the units of length, energy, and magnetic field; $\gamma=1$ is the magnetic field at which the diamagnetic energy is equal in magnitude to the Coulomb energy. [For the free hydrogen atom $\gamma=1$ would correspond to $H_z=2.35\times10^9$ $G$, but for a donor impurity it would be reduced by a factor $(m^*/m_0\epsilon)^2$ $\sim10^{-3}$ or less]. $\epsilon$ is the static dielectric constant, and $m^*$ the (scalar) effective mass. For purposes of comparison with experiment we choose $m^*$ $=0.3m_0$ and $\epsilon=11.4$. (The value $m^*=0.3m_0$ has been chosen so as to give the same binding energy as that obtained in the single valley case with anisotropic masses.) In writing (1) we have omitted relativistic terms, which yield a spin-dependent polarizability. These terms have been shown to be negligible for most purposes.[6] To calculate the polarizability we introduce an additional electric-field term

$$\mathcal{H}_1 = -e a^* E_t t / R^* = -\xi t \ , \tag{3}$$

where $t$ stands for $z$ or $x$, parallel or perpendicular to the direction of the magnetic field $H$. The Hamiltonian in the presence of an external magnetic and electric field is therefore given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 . \tag{4}$$

The polarizability $\alpha$ is defined by

$$E(H_z, \xi) = E(H_z, 0) - \tfrac{1}{2}\alpha\xi^2 , \tag{5}$$

i.e.,

$$\alpha = 2 \lim_{\xi\to 0} \frac{E(H_z, 0) - E(H_z, \xi)}{\xi^2} . \tag{6}$$

Depending on the direction of $\vec{\xi}$ we obtain the components $\alpha_\perp$ if $\vec{\xi}\perp\vec{H}$, and $\alpha_\parallel$ if $\vec{\xi} \parallel \vec{H}$.

We now seek the eigenfunctions of the Hamiltonian in Eq. (4). We write the solution $\psi(\vec{r})$ as

$$\psi(\vec{r}) = \sum_{i=1}^{n} f_1(r) Y_{l_i m_i}(\theta, \varphi) , \tag{7}$$

i.e., we expand it in terms of spherical harmonics. In the absence of any external field, $l$ and $m$ are good quantum numbers and therefore there would be only one angular term in the expansion (7). Once the magnetic field is introduced, $l$ is no longer a good quantum number but $m$ and parity still are. Therefore for the ground state, the sum in (7) will contain only terms with fixed $m$ and even $l$. When the electric field is turned on, parity is no longer a good quantum number and $m$ will still be if the electric field lies in the same direction as the magnetic field, otherwise even $m$ is no longer a good quantum number and the sum in (7) will contain terms with any $l$ and $m$. In order to evaluate the expectation value of the Hamiltonian (4), we must calculate its matrix elements in the basis (7). To take full advantage of the present method, it is convenient to rewrite (4) in terms of irreducible components of tensor operators whose effect on the basis functions (7) can be calculated using standard angular-momentum relationships.[12] Equation (1) can be rewritten as

$$\mathcal{H}_0 = -\nabla^2 - 2/r + \tfrac{1}{12}\gamma^2\left(2r^2 - \sqrt{\tfrac{2}{3}}\, T_0^2\right) , \tag{8}$$

where $T_m^l$ represents the $m$th irreducible component of the tensor of rank $l$, as defined by Edmonds.[12] Obviously here

$$T_0^2 = \sqrt{\tfrac{3}{2}}\,(2z^2 - x^2 - y^2) = \sqrt{\tfrac{24}{5}\pi}\, r^2 Y_{2,0} . \tag{9}$$

The electric field term can be written

$$\mathcal{H}_1 = -\xi z = -\xi T_0^{(1)} = -\xi\sqrt{\tfrac{4}{3}\pi}\, r Y_{1,0} \tag{10}$$

or

$$\mathcal{H}_1 = -\xi x = -\xi\frac{T_{-1}^1 - T_1^1}{\sqrt{2}} = -\xi\sqrt{\tfrac{4}{3}\pi}\, r\, \frac{Y_1^{-1} - Y_1^1}{\sqrt{2}} . \tag{11}$$

The following relationships can therefore be used

$$\left(\nabla^2 + \frac{2}{r}\right) f(r) Y_{l,m} = Y_{l,m} \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2}{r}\right) f(r) , \tag{12}$$

$$T_0^2 f(r) Y_{l,m} = \sqrt{6} f(r) r^2 \sum_{l'} [(2l'+1)(2l+1)]^{1/2} \times \begin{pmatrix} 2 & L & L' \\ 0 & m & m' \end{pmatrix} \begin{pmatrix} 2 & L & L' \\ 0 & 0 & 0 \end{pmatrix} (-1)^{m'} Y_{l',m'} . \tag{13}$$

$$T_{m''}^1 f(r) Y_{l,m} = f(r) r \sum_{l'm'} [(2l'+1)(2l+1)]^{1/2} \times \begin{pmatrix} 1 & L & L' \\ m'' & m & m' \end{pmatrix} \begin{pmatrix} 1 & L & L' \\ 0 & 0 & 0 \end{pmatrix} (-1)^{m'} Y_{l',m'} . \tag{14}$$

Using these relationships we can treat exactly and analytically the angular part of the matrix elements of (4) in the basis (7). One is therefore left with systems of radial differential equations for the $f_i(r)$. These systems can be solved very accurately by making the following ansatz,

$$f_i(r) = \sum_{j=1}^{M} C_{ij} e^{-\eta_j r} . \tag{15}$$

The eigenvector coefficients $C_{ij}$, and the corresponding eigenvalues are obtained by solving the secular determinant of

$$\sum C_{ij}(H_{ij} - ES_{ij}) = 0 . \tag{16}$$

The size of the secular determinant in (16) is $N \times M$, where $N$ is the number of terms in (7) and $M$ the number of terms in (15). The parameters $\eta_j$ are not treated as variational parameters. With a sufficiently large number of terms ($M$) describing the physically interesting spatial range of the wave function, the specific choice of the $\eta_i$'s does not matter, as discussed more extensively in Sec. IV. We also note that it is not necessary to include any powers of $r$ with each exponential in (15).

## III. MODEL HAMILTONIAN FOR DONOR IMPURITIES

The first successful theoretical investigation of donor spectra in semiconductors was given by Kohn and Luttinger[13] using the EMA. In indirect-gap

TABLE I. Values of the parameter $K$ (in atomic units), which are obtained by requiring that the calculated donor binding energies equal the experimental ones. We have used $\epsilon = 11.4$ and $m^* = 0.3m_0$. The energy unit is meV.

| Material | $K$ | $E_b$ (calc.) | $E_b'$ (expt.) |
|---|---|---|---|
| Hydrogenic | $\infty$ | 31.41 | |
| P | 0.574 | 45.45 | 45.47 |
| As | 0.515 | 53.70 | 53.69 |
| Sb | 0.608 | 42.68 | 42.69 |

materials, the multivalley nature of the conduction band gives rise to a multiplet structure of the donor-impurity ground state, because the intervalley components of the impurity potential remove the degeneracy between the zero-order states obtained independently for each valley.[8] This "valley-orbit" interaction is quite substantial, as it increases the binding energy of the ground state by about 35% for P in Si,[14] and should therefore be included in the theoretical description of these states. An accurate description of this effect is very difficult, however, as has long been appreciated and recently emphasized anew.[11] Furthermore, the donor-binding energy depends on the given impurity, e.g., P, Sb, and As donors in Si have different binding energies.[14] A proper analysis of these "chemical shifts" is not yet available, and we do not attempt one here. Instead, we use the simplest formulation possible which incorporates in some average way the effects described previously. We do so by introducing a phenomenological impurity dependent potential of the form

$$V(r) = -(e^2/\epsilon r)[1 + (\epsilon - 1)e^{-Kr}] \quad . \tag{17}$$

The coefficient $K$ determines the strength of the screening of the potential $V$. In fact when $K \to \infty$ Eq. (17) reproduces the static screened potential, while for $K = 0$ it gives the unscreened Coulomb potential. The value of $K$ for each impurity is determined by requiring the calculated binding energy to agree with the observed one for that impurity. The use of this potential does not complicate the solution of the problem because it does not involve any new type of integrals. In Table I we give the values of $K$ for As, P, and Sb in silicon.

TABLE II. Energy of the hydrogen ground state as a function of the magnetic field. Comparison with Cabib *et al.* (Ref. 2) is also shown. The energy unit is the effective Rydberg.

| $\gamma$ | $E_{1s}$ (present) | $E_{1s}$ (Cabib *et al.*) |
|---|---|---|
| 0.0 | −1.000 00 | −1.000 00 |
| 0.1 | −0.995 05 | −0.995 08 |
| 0.2 | −0.980 76 | −0.980 76 |
| 0.3 | −0.958 37 | −0.958 41 |
| 0.4 | −0.929 21 | −0.929 23 |
| 0.5 | −0.894 42 | −0.894 47 |
| 0.6 | −0.854 92 | −0.854 94 |
| 0.7 | −0.811 45 | −0.811 42 |
| 0.8 | −0.764 57 | −0.764 57 |
| 0.9 | −0.714 74 | −0.714 73 |
| 1.0 | −0.662 34 | −0.662 41 |
| 1.5 | −0.370 71 | −0.370 76 |
| 2.0 | −0.044 43 | −0.044 50 |
| 2.5 | 0.304 93 | 0.304 90 |
| 3.0 | 0.670 94 | 0.670 87 |
| 4.0 | 1.438 4 | 1.438 4 |
| 5.0 | 2.239 2 | 2.239 2 |

TABLE III. Ground-state binding energy for P, As, and Sb donor impurities in Si, using the model potential described in Sec. III. The energy unit is the effective Rydberg.

| $\gamma$ | P | As | Sb |
|---|---|---|---|
| 0.0 | 1.447 29 | 1.709 83 | 1.359 08 |
| 0.2 | 1.437 10 | 1.702 09 | 1.347 75 |
| 0.4 | 1.408 21 | 1.679 79 | 1.315 86 |
| 0.6 | 1.364 01 | 1.644 95 | 1.267 53 |
| 0.8 | 1.307 69 | 1.599 70 | 1.206 41 |
| 1.0 | 1.241 70 | 1.545 83 | 1.135 23 |
| 2.0 | 0.817 36 | 1.188 07 | 0.682 82 |
| 3.0 | 0.301 28 | 0.740 47 | 0.138 00 |
| 4.5 | −0.265 73 | 0.241 07 | −0.457 52 |
| 5.0 | −0.865 67 | −0.292 55 | −1.085 62 |
| 10.0 | −4.123 49 | −3.237 00 | −4.479 14 |

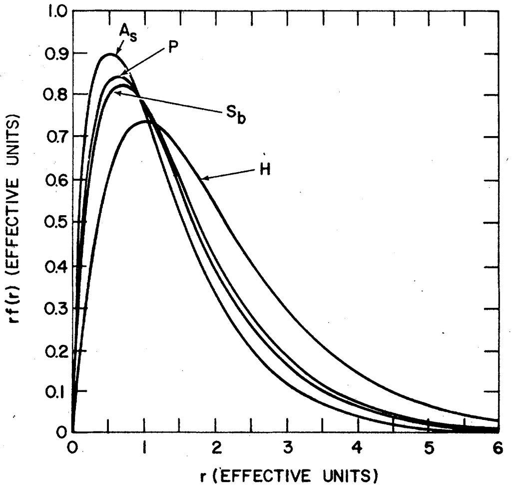

FIG. 1. Plot of the calculated radial part of the ground-state wave function [actually $r \times f(r)$] as a function of $r$ in the absence of applied fields for various impurities in Si.

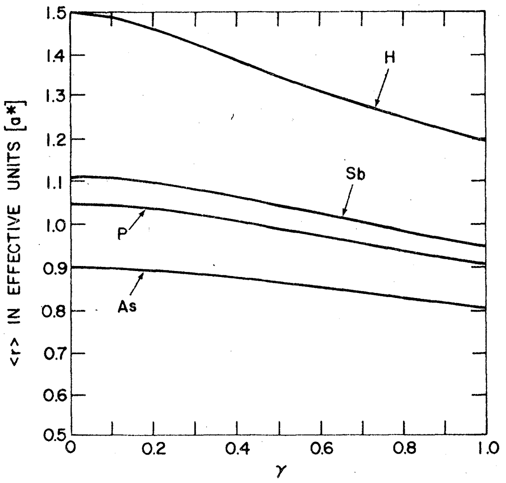

FIG. 2. Plot of the expectation value of $r$, $\langle r\rangle$, as a function of reduced magnetic field for H, P, As, and Sb impurities in Si.

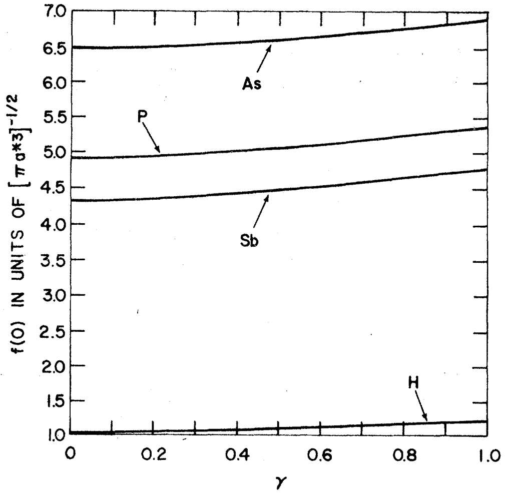

FIG. 3. Calculated magnitude of the radial wave function at the origin for various impurities in Si as a function of reduced magnetic field.

## IV. NUMERICAL RESULTS AND DISCUSSION

We first address the question of convergence of the binding energy as a function of the basis functions in (15). In principle, the exponents $\eta_i$ should be allowed to change in a variational way and to depend on any given state. In practice, however, as we have previously seen,[15] the $\eta_i$ can be fixed and not considered as variational parameter, if one chooses a sufficient number of terms in (15) and if the $\eta_i$'s are selected in a sensible way. We have seen that it suffices (i) to include 15 terms in (15), and (ii) to choose the largest and smallest $\eta_i$ to be 50 and 0.05, respectively, with the intermediate ones chosen in geometrical progression, to insure convergence in eigenvalues to better than one part in $10^6$. The next question regards how many terms should be included in (7). This number obviously increases with the strength of the magnetic field. In Table II the ground-state binding energy, using six terms in (7), is given. In the last column the results of Cabib *et al.*[2] (CFF) are also given for comparison. We see that our results reproduce accurately the sophisticated calculations of CFF for $\gamma$'s up to 5. We have also compared our results for $\gamma$ up to 100 with the results of Baldereschi and Bassani[5] and the agreement is excellent, thus showing that the present method can handle any value of the magnetic field. In all the subsequent calculations we shall always use up to $L_{\max}=10$ (i.e., six terms) in the expression. In Table III we report the magnetic field dependence of the ground state binding energy for P, As, and Sb in Si, respectively, using the model potential described in the previous section. In Fig. 1 we show the ground-state wave function in the absence of any external field for the four cases considered in this paper. The expectation value of $r$ for the ground state, as a function of the reduced magnetic field, is shown in Fig. 2, for the various impurities while the value at the origin, $|\psi(0)|$ is given in Fig. 3.

To determine the polarizability $\alpha$ we calculate the binding energy using a very small value for the electric field and then use expression (6). To ensure that the electric field is indeed "infinitesimal," that is, only virtually perturbs the wave functions, we have performed calculations with $\xi = 0.05, 0.025, 0.01$ with essentially the same results (to four significant figures). The introduction of

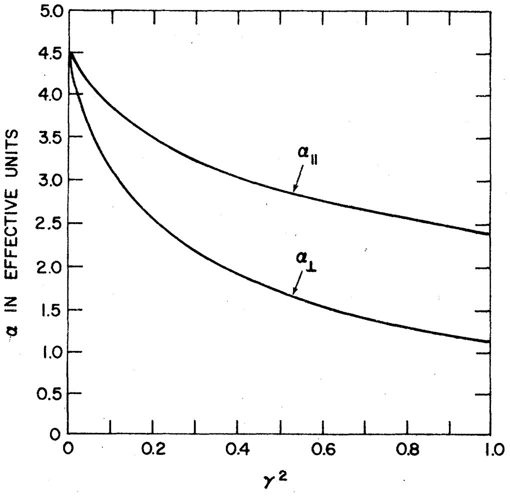

FIG. 4. Calculated polarizability components in effective units as a function of $\gamma^2$ for the hydrogenic impurity in Si.

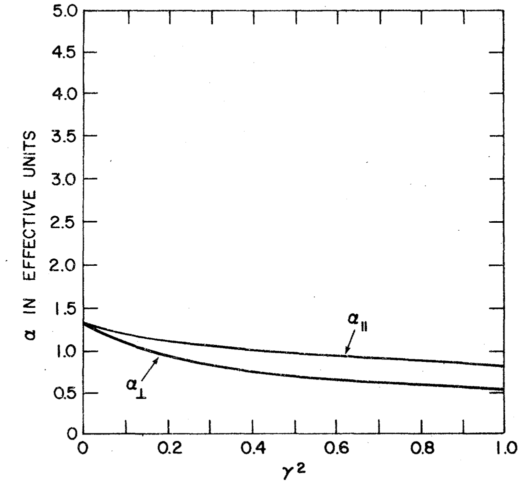

FIG. 5. Same as Fig. 4 for the P impurity.

the electric field requires the odd $L$ terms in expression (7) and in the calculation we have used all odd terms up to $L_{\max}+1$. For $H_z = 0$, the calculated polarizability $\alpha$ for hydrogen can be compared with the exact value.[16] We obtain for $\alpha$ a value which compares very well (i.e., to four significant figures) with the exact value $\frac{9}{2}$. In Fig. 4 we show the magnetic field dependence of $\alpha_\perp$ and $\alpha_\parallel$. These results compare reasonably well with those obtained in a previous paper in the low $\gamma$ region by one of us (D.L.D.), and in addition, they are valid also for large $\gamma$.

In Figs. 5–7 the polarizabilities for P, As and Sb are given and we see that the magnetic-field dependence gets weaker with increasing binding energy. This is reasonable since the wave function becomes more localized with increasing binding energy and therefore the external fields are less effective in perturbing the wave functions.

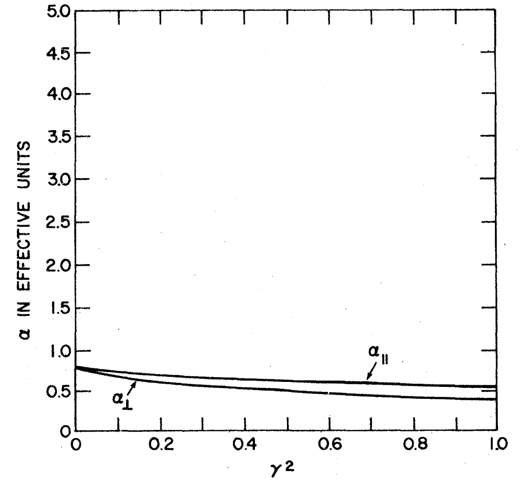

FIG. 6. Same as Fig. 4 for the As impurity.

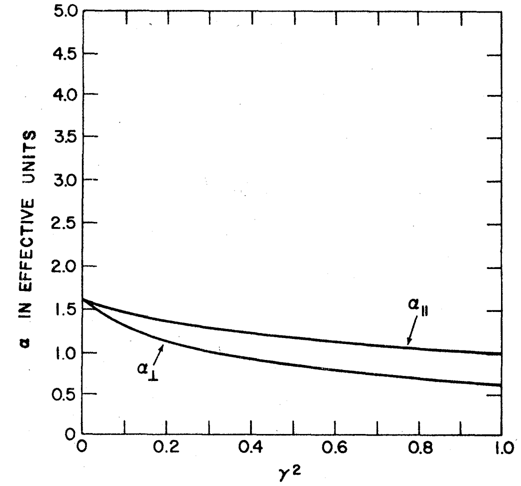

FIG. 7. Same as Fig. 4 for Sb impurity.

The comparison with experiment is to be performed with caution since we have used here a crude approximation for the description of the donor-impurity dependence. The calculated decrease of $\alpha$ for $H_z = 0$ in going from Sb to As is in agreement with observation. In fact, we predict $11\times10^5 a_0^3$ for Sb, $8.2\times10^5 a_0^3$ for P, $4.9\times10^5 a_0^3$ for As, while the experiment gives $21\times10^5 a_0^3$, $16\times10^5 a_0^3$, and $6.7\times10^5 a_0^3$, respectively. Also in agreement with experiment is the weaker dependence of $\alpha$ with magnetic field in going from Sb to As. The calculated absolute value of these dependences however is quite different from the observed ones. Specifically, the calculated dependences are much weaker than for the hydrogenic atom which in turn are much weaker than the experimental ones. Even though these results are obtained using a crude approximation, the fact that the experimentally observed dependence of $\alpha$ on $H_z$ is much larger than even the hydrogenic case is puzzling. Ideally one should perform calculations using a more realistic model for the donor impurities which include a proper description of the electron anisotropy, intervalley coupling, and central-cell effects but in fact one would expect that, since the observed binding energies for the various donors are always greater than for the hydrogenic case, any calculation, even a more sophisticated one, would give the same qualitative results as those obtained here. More experimental information is also required to interpret the disagreement between theory and experiment.

## ACKNOWLEDGMENTS

We are indebted to T. G. Castner for useful discussions. This work was supported in part by the AFOSR under Contract No. F49620-77-C-005.

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