Geschw. [km/sec]	$E_{\text{kinet.}}$ [eV]	σ [10^{-17} cm^2]	λ [10^{18} cm]
50	13	3,16	0,32
100	52	0,79	1,27
200	208	0,178	5,6
300	470	0,0556	18,2
400	835	0,0416	24,0

Tab. 1.

Die hier ausgeführte Näherungsrechnung läßt also keinen anderen Schluß zu, als daß neutralisierte Sonnenwindteilchen beim Übergang vom interplanetaren zum interstellaren Raum nicht wesentlich thermalisiert werden, bevor sie den nächsten Fixstern erreichen. Das stimmt überein mit der Annahme von BLUM und FAHR[3], daß die elastischen H-H Stoßquerschnitte gegen die H-H$^+$ Ladungsaustauschquerschnitte in einem Modell für das Verhalten des interstellaren Wasserstoffs vernachlässigt werden können.

[3] P. W. BLUM u. H. J. FAHR, Astron. Astrophysics **4**, 280 [1970].

Molecular Diamagnetism: Uncoupled Calculations for Two Center Systems

B. M. LUDWIG and J. VOITLÄNDER

Sektion Physik und Physikalisch-Chemisches Institut der Universität München

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For Σ^1 molecules constructed from first row elements of the Periodic Table computations of the diamagnetic susceptibility and the nuclear magnetic shielding constants are reported. The method used is a gauge invariant approximation to the gauge dependent "uncoupled" perturbation theory in the Hartree-Fock scheme; the groundstate description considered is provided by the best limited MO functions.

Some emphasis is placed on methodological aspects and the role of π-electrons in this context; acceptable overall agreement with experiment is achieved, especially for the mean diamagnetic susceptibility. The phenomenon of antishielding occurring for fluorine and nitrogen nuclei is shown to depend critically upon the nodal structure of the state. A similar behaviour of the induced current density is not predicted by the semiclassical Thomas-Fermi theory, for which results are obtained too. This theory fails for principle reasons to explain the linear magnetic response of nonspherical systems.

I. Introduction

The basic quantummechanical formulation of the diamagnetic properties of molecules proceed via second order perturbation theory[1]. The original approaches [2] use Rayleigh-Schrödinger perturbation calculus and express the second order energies E_2

$$\text{a)}\ E_2^{\chi} = -\boldsymbol{B}\hat{\boldsymbol{\chi}}\boldsymbol{B}, \quad \text{b)}\ E_2^{\sigma} = \boldsymbol{B}\hat{\boldsymbol{\sigma}}\boldsymbol{\mu}_N \qquad (1)$$

$\boldsymbol{\mu}_N$ being the nuclear dipole, $\boldsymbol{B}$ the external field, $\hat{\boldsymbol{\chi}}$ and $\hat{\boldsymbol{\sigma}}$ the susceptibility and shielding tensors respectively, as infinite series, which appear, except for the trivial case of atoms, not to be susceptible of actual evaluation.

There have been two perturbation variation studies of these quantities covering the range of molecules to be considered here, one of which — Lipscombs[3] calculations by the perturbed or coupled Hartree-Fock method — seems to be adequate, but rather involved and time consuming. A residual gauge dependence still subsists. The other[4] uses different methods for the susceptibility and shielding constants, which however are manifestations of one single effect, the intramolecular Faraday effect. The work presented here may be thought of as being an extension and simplification of these procedures. It includes Thomas-Fermi molecules too and may contribute to the discussion of the role played by π-electrons.

Reprint requests to: B. M. LUDWIG, c/o Phys.-Chem. Institut der Universität, *D-8000 München 2*, Sophienstr. 11.

[1] J. I. MUSCHER, Adv. Magn. Res. **2**, 177 [1966]. — D. E. O'REILLY, Progr. NMR Spectrosc. **2**, 1 [1967].

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II. Theoretical Remarks

We are going to use a simple pictorial language to describe the effects exerted by an external magnetic field upon a diamagnetic system, which by definition here is a system without permanent moment. The (static) field $\boldsymbol{B}$ is said to produce, when switched on, a classical Faraday effect in the electronic charge cloud of the (Born-Oppenheimer) molecule, described by the occurrence of a current density distribution proprotional to the field. This current in turn gives rise to an induced secondary field distribution over the range of the electron cloud, particular values of which are seen by the nuclei. They experience thus an alteration of the external field, the nuclear shielding measured in NMR experiment. A second consequence is the appearance of an induced moment of the entire molecule, whose sign is still a subject of investigation[5].

Let $\boldsymbol{j}^{\alpha}$ denote the current density induced in the space fixed molecule by an external field along the cartesian coordinate α, then classical relations may be used to give:

$$\chi^{\alpha\beta} = - \left.\frac{\partial^2 E}{\partial B_\alpha \partial B_\beta}\right|_{\boldsymbol{B}=0} = \tfrac{1}{2}\, \mu_0 L \int \mathrm{d}\tau [\boldsymbol{j}^{\alpha} \times \boldsymbol{r}]_\beta \,, \tag{2a}$$

$$\sigma^{\alpha\beta}(\boldsymbol{R}) = \left.\frac{\partial^2 E}{\partial B_\alpha \partial \mu_\beta}\right|_{\boldsymbol{\mu}=\boldsymbol{B}=0} = \frac{\mu_0}{4\pi} \int \mathrm{d}\tau \left[\frac{\boldsymbol{j}^{\alpha} \times (\boldsymbol{r}-\boldsymbol{R})}{|\boldsymbol{r}-\boldsymbol{R}|^3}\right]_\beta , \tag{2b}$$

(Giorgi units),

for the tensor elements of the molar susceptibility and the shielding at the position $\boldsymbol{R}$.

As all the formulas displayed may be converted by some calculus and changes in notation into the more abstract quantummechanical constructs[6] we are entirely authorized to use a classical language.

The main lines of analysis and a first application to the hydrogen molecule have been given elsewhere [7]; the presence of more than two electrons requires a nontrivial extension however. We shall limit us to the closed shell case of the Hartree-Fock approximation.

Much of the work done on the linear magnetic response of molecules may concisely be summarized by and derived from the steady state condition

$$\operatorname{div} \boldsymbol{j} = 0 \,. \tag{3a}$$

We treat the one electron case first. Let $\boldsymbol{A}$ denote the vectorpotential of a given homogeneous field $\boldsymbol{B}$, Ψ the wavefunction, the orbital of the electron, when the field is present

$$\Psi = \Phi + (i\, e/\hbar)\, b \,,$$

and Φ the (real) wavefunction of the electron of the free system. The current density is written as

$$\boldsymbol{j}[\boldsymbol{B}] = e\{(\hbar/m) \operatorname{Im}(\Psi^* \nabla \Psi) + \gamma \,|\Psi|^2 \boldsymbol{A}\} \,, \tag{4}$$

$\gamma = e/m$; e, m: charge and mass of the electron.

We are interested only in that part of the currents, which are proportional to the applied field. Then:

$$\boldsymbol{j} = e\gamma \cdot \{\Phi \nabla b - b \nabla \Phi + \Phi^2 \boldsymbol{A}\} \,. \tag{5}$$

A) Assume, that there is a gauge function f for $\boldsymbol{A}$ that allows to write:

$$\boldsymbol{j} = e\gamma n \boldsymbol{A}', \quad \boldsymbol{A}' = \boldsymbol{A} + \nabla f \tag{6}$$

with: $n = |\Phi|^2$.
Equation (3 a) reads now

$$n \Delta f + \nabla n (\nabla f + \boldsymbol{A}) = 0 \,, \tag{3b}$$

determining f if boundary conditions are specified. Precisely the same equation follows within the framework of the semiclassical Thomas-Fermi model [7,8].

B) Comparison of the Eqs. (6) and (5) shows that $f \sim b/\Phi$, i. e. the imaginary part of the wavefunction defines a gauge transformation appropriate to the orbital geometry, supposing here $\Phi \neq 0$ always. Equation (3 a) gives now:

$$\Delta b - b\,(\Delta\Phi/\Phi) + 2\,\boldsymbol{A} \nabla \Phi = 0 \,. \tag{3c}$$

C) Equation (3 c) is nothing but the first order perturbation problem for the Hamiltonian:

$$\mathscr{H} = \mathscr{H}_0 + i\,\mathscr{H}_1 = -\frac{\hbar^2}{2m} \Delta + V - \frac{i e \hbar}{m} \boldsymbol{A} \cdot \nabla \,. \tag{7}$$

Substituting:

$$V - E_0 = \frac{\hbar^2}{2m} \frac{\Delta\Phi}{\Phi} \tag{8}$$

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[5] W. N. Lipscomb and R. Hegström, Rev. Mod. Phys. **40**, 354 [1968]. — [5a] R. M. Stevens, W. N. Lipscomb, J. Chem. Phys. **40**, 2238 [1964].

[6] C. P. Slichter, Principles of Magn. Resonance, Harper & Row, New York 1963.

[7] B. M. Ludwig and J. Voitländer, Mol. Phys. **16**, 405 [1969]; Z. Naturforsch. **24a**, 471 [1969].

[8] T. K. Rebane, Sov. Phys. JETP **11**, 694 [1960]. I. Espe, Phys. Rev. **103**, 1254 [1956].

from the zero order equation into:

$$(\mathscr{H}_0 - E_0)\frac{e}{\hbar}\, b = \mathscr{H}_1 \Phi \tag{9}$$

we are back to Eq. (3c).

D) Writing the perturbed part of the orbital as being proportional to the unperturbed part is sometimes referred to as the *f*-function technique[5,9]. With Eq. (7) and $f \sim b/\Phi$ this formulation again is an expression of the steady state condition. The equivalence of this technique and the gauge transformation theories has been noticed in the literature[5].

To the different formulations there exist variational principles which physically mean the minimization of the magnetic second order energy, which is the energy of the induced moment in the external field. Equation (3c) is the condition of stationarity of the integral

$$\langle (\nabla b)^2 + b^2\,(\Delta\Phi/\Phi) + 4\,\boldsymbol{A}\, b\, \nabla\Phi \rangle\,. \tag{10a}$$

E) Formulation in terms of the *f*-function is useful only if Φ does not vanish, since otherwise the variation integral

$$\langle n\,(\nabla f)^2 + (2\,m/e^2)\,\boldsymbol{A}\cdot\boldsymbol{j} \rangle \tag{10b}$$

contains diverging terms from $(\nabla f)^2$.

This difficulty may be overcome, if detailed information on the nodal structure of Φ is given. Write Φ in the product form

$$\Phi = \psi\, u\,, \tag{11}$$

$u \neq 0$ and square integrable, but arbitrary otherwise, and similarly:

$$b = g\cdot u\,, \tag{12}$$

g being to be determined. Then:

$$\boldsymbol{j} = e\,\gamma\, u^2\,(\psi\,\nabla g - g\,\nabla\psi + \psi^2\,\boldsymbol{A}) \tag{13}$$

and

$$\begin{aligned}\operatorname{div}\boldsymbol{j} = 0 &= u^2\,\Delta g + \nabla(u^2)\,\nabla g\\ &\quad - g\left(\frac{\Delta\psi}{\psi}\,u^2 + \frac{\nabla\psi}{\psi}\,\nabla(u^2)\right) + 2\,\boldsymbol{A}\,\nabla\Phi\cdot u\,. \end{aligned}\tag{3d}$$

The quantity in brackets, Ω, does diverge at the nuclei only as does $\Delta\Phi/\Phi$, the local kinetic energy density. The equivalent variation integral is

$$\langle u^2\,(\nabla g)^2 + g^2\,\Omega + (2\,m/e^2)\,\boldsymbol{A}\cdot\boldsymbol{j} \rangle\,. \tag{10c}$$

This method will be referred to as the *g*-function technique.

F) There exists a closely related variation problem for the phase of the wavefunction[10,11], which to use is less direct, as the complete phase in general is a many-valued function connected with the structure of angular momentum; this many-valued part however is not related to the field.

To keep out of the calculations the potentials by replacing them by the local kinetic energy is in fact quite general and may be used for all types of one electron perturbations. Being of no influence for the exact treatment, it emphasises the errors in Φ in approximate calculations of molecular properties. This may be considered to be an advantage, if the purpose is to test closely existing wavefunctions rather than to bring about values most adjacent to experiment. For our particular concern, this term comes out quite naturally from the condition $\operatorname{div}\boldsymbol{j} = 0$.

What has been said above for the one electron case may at once be interpreted as a formulation in an n-particle configuration space. As we intend to work on an orbital picture, the point is now to break down all the expressions to orbital formulas; we slip this point however, since the general case[9] as well as the case of shielding constants[1,12] has been treated in the literature. The result is, provided we neglect the selfconsistency requirement to second order in the total Hartree-Fock energy that all of the above formulas are to be interpreted as orbital equations, the total effects being orbital superpositions. These neglected terms are specific to the SCF-approximation and the admissibility of this neglect remains to be discussed — any theory using local potentials only will not contain such terms. In keeping these "nonlocality" terms, the coupled Hartree-Fock procedure as presented by Lipscomb is reobtained.

The total current density is given by:

$$\boldsymbol{j} = \sum_{\text{occ. orb.}} \boldsymbol{j}_i$$

with $\boldsymbol{j}_i$ from Eqs. (6) or (13). This quantity is invariant with respect to unitary orbital transforma-

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tions; further, if the set $\{\Phi_i\}$ of groundstate orbitals is an orthonormal one, the perturbed orbitals will be orthonormal to first order.

III. σ- and π-Orbitals in Two Center Systems

Consider the diatomic $^1\Sigma$ molecules made up from elements of the first row of the periodic table.

Introduce cartesian coordinates (x, y, z) centered at the midpoint of the internuclear distance, the y-axis coinciding with the symmetry axis as well as confocal ellipsoidal coordinates (μ, ν, φ) defined by, cf. Fig. 1,

$$\mu = \frac{1}{2R}(r_a + r_b), \quad \nu = \frac{1}{2R}(r_a - r_b), \quad \cos\varphi = \frac{x}{\varrho}. \tag{14}$$

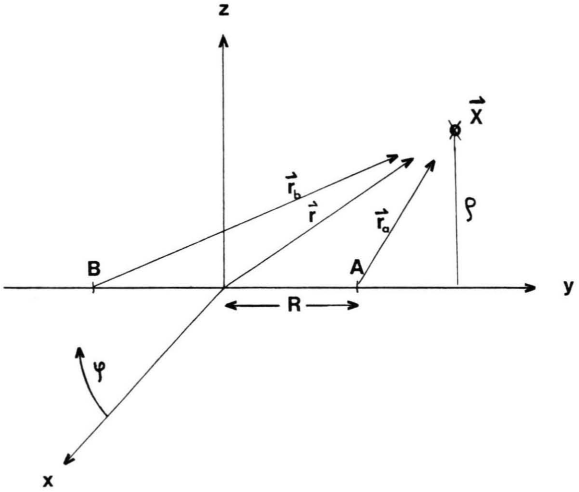

Fig. 1. Coordinate systems.

The molecular orbitals (MO's) may be classified as σ- and π-orbitals. Except the 1σ orbital, which is lowest in energy, all of them do have nodes. In order to apply the g-function technique, these nodes must be known explicitly. Further, across the nodes, the kinetic energy density, $\Delta\Phi/\Phi$, should remain finite. This requirement however is not met by the approximate zero-order MO's we have treated, namely the BLMO functions[13]; more sophisticated wavefunctions do show the same defect. In spite of this irregular behaviour it would still be possible to use the principal values of certain integrals; together with the numerical search for the nodes this procedure will become somewhat clumsy.

For these reasons the f-function technique has been applied to all of the σ-orbitals. Mathematically, this means a restriction of the class of functions admitted to the variation of the integral (10c); physically, no current is allowed to flow across the nodes.

A Fourier type analysis of the angular dependence of the steady state condition shows that f is to be proportional to $\cos\varphi$. We write, then,

$$f = \frac{Rx}{2} \sum_{q,p \geq 0} C^1_{pq}\, \mu^p \gamma^q \tag{15}$$

and are left with some integrations and a system of linear equations, that have been considered for up to fifty parameters C. Results will be discussed below.

Now, concerning the π-MO's, they do have very simple nodes, which present the important additional feature of containing the nuclei in contrast to the situation found for the σ-MO's. This special construction of the π-nodes may be thought to be responsible for the low field NMR shifts in certain compounds, more particularly, the antishiedling observed for N and F nuclei. This does not entail the van Vleck paramagnetism to become overwhelming. The situation is schematically illustrated in Fig. 2, which shows two charge concentrations

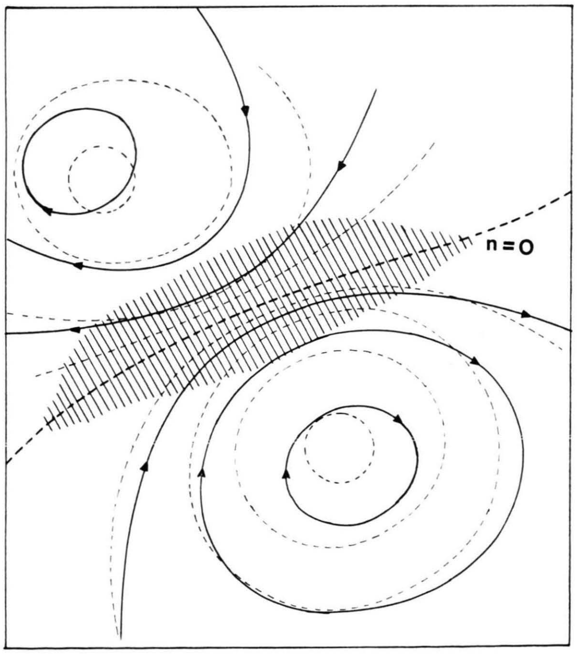

Fig. 2. Schematic construction of antishielding. General diamagnetic and local paramagnetic behaviour (shaded). – – –: Isodensity contours.

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[13] B. J. Ransil, Rev. Mod. Phys. **32**, 245 [1960].

separated by a nodal plane. Each of the charge clouds undergo a diamagnetic circulation (according to Lenz' rule) but in between them there may appear a region containing currents, that aid the external field. The node thus plays an important role as a structural element.

Apply this idea to the π_x-orbital of the hydride NH or FH. Within the BLMO description, this is simply the p_x-orbital of the heavy nucleus. Ignoring the molecular context, this orbital is degenerate with a p_y-orbital (pertaining to a spherical symmetric Hamiltonian); consequently Larmor's theorem should be applied, leaving no high frequency term. However, divide the whole space along the nodal plane of this p_x-function ($\boldsymbol{B}$ pointing along the z-axis) and vary the f-function for each of the halfspaces separately, thus taking into account the nonspherical character of the situation. Choose f to be approximately

$$f = -\gamma (B/2)\, x_0\, y\,, \quad p_x \sim x\, e^{-\xi r}, \tag{16}$$

where x_0 is now the variation parameter.

The result for the two subspaces is $\xi \cdot x_0 = \pm 15/8$, leading to $\sigma^{pxx}/\sigma^{dxx} = -25/16$, i.e. antishielding at the nuclear site. The currents conform to the pattern of Fig. 2; in the true two-center case the result is more involved.

The angular dependence of g is recognized from Eq. (3d) as

$$g = g_0(\mu, \nu) + g_2(\mu, \nu) \cos 2\varphi\,, \tag{17a}$$

which is reformulated as

$$g = V(\mu, \nu) \sum C^0_{pq}\, \mu^p \nu^q + R(x^2 - z^2) \sum C^2_{pq}\, \mu^p \nu^q \tag{17b}$$

when the field is parallel to the nodal plane, and

$$g = g_2(\mu, \nu) \sin 2\varphi \tag{17c}$$

when the field is perpendicular to the node, g_2 being the same function in both cases. The factor $V(\mu, \nu)$ is inserted for convenience, since we are effectively using truncated basis sets, we are free to choose this factor, finally fixed as $R y_a y_b$. This corresponds to some extent to the excitation $p_x \rightarrow p_y$.

It is the first term of Eq. (17b) that is to describe the currents across the nodes, thus modifying the pattern of Eq. (16) and producing large low field shifts, cf. Fig. 3, 4.

All occuring integrals may be expressed by the exponential integral and related functions. For the integrals containing inverse powers of r_i of the relation (2b), no Barnett-Coulson expansion is needed; the elements of these matrix elements may be generated in a stable recursive fashion.

IV. Results and Discussion

The relevant results of the outlined calculations are presented in Tables 1, 2 and 3. Table 1 contains the ,,diamagnetic'' parts and the yy-tensorelements, i.e. the properties, if $\boldsymbol{B}$ is parallel to the molecular axis; Tables 2 and 3 quote the results of the mean susceptibilities and shielding constants at three different levels of sophistication:

A) Taking the complete electronic density as constituting an approximation to the semiclassical densities of the Thomas-Fermi model. This case is covered by the expressions (3b) and (10b).

B) Using the restricted variation principle for the f-function for each orbital separately.

C) Treating the π-MO's by means of the g-function. This gives the best values of the present work.

For both tensors. $\hat{\tau}$, $\hat{\tau} \in (\hat{\chi}, \hat{\sigma})$, we have

$$\bar{\tau} = \tfrac{1}{3}\, \boldsymbol{Tr}\, \hat{\tau}\,, \quad \tau^{\alpha\beta} = 0 \quad \text{if} \quad \alpha \neq \beta;$$

$$\Delta\tau = \tau_{\parallel} - \tau_{\perp} = \tfrac{3}{2}\,(\tau_{\parallel} - \bar{\tau})\,.$$

The susceptibility units are m^3/mole (rationalized) throughout. For the low frequency part of χ, depending directly on $\boldsymbol{A}$, the vectorpotential is chosen around the origin; as regards the shielding, conforming to standard notation the homogeneous circulation around the nucleus under consideration is used.

Resently, values have been reported both experimentally[14] and form a comfortable perturbed Hartree-Fock calculation[15] for the anisotropy of the susceptibility in CO:

	Experiment	Pert. SCF	This work
$\Delta\chi_{\mathrm{CO}}$	-1.03 ± 0.1	-0.88 -0.905	-0.57

Much of the error here comes from the low value of $\chi_{\parallel} = -2.10$ (Table 1), the near Hartree-Fock value[15] being -2.26. Combining this number with our variational solution, the anisotropy is obtained to be $\Delta\chi = -0.81$. This is a true defect of the

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[15] R. M. Stevens and M. Karplus, J. Chem. Phys. **49**, 1094 [1968].

A B	H	He	Li	Be	B	C	N	O	F	Ne
H	-0.504 -0.464 32.36 27.85		-1.88 -1.18 39.52 28.12		-2.57 -1.39 57.98 33.97		-2.03 -1.55 74.71 32.76		-1.75 -1.02 110.7 44.80	
He										
Li	107.9 101.5		-6.62 -3.87 112.5 103.9						-4.33 -2.13 157.7 106.4	
Be				-6.26 -3.14 168.1 153.0						
B	209.6 199.0								-3.92 -2.09 268.8 209.8	
C						-3.93 -2.55 305.4 277.9		-4.44 -2.10 324.4 271.0		
N	333.4 343.1						-3.64 -2.05 384.5 339.3			
O						441.2 408.1				
F	481.6 482.9		492.4 447.9		504.8 481.1				-4.92 -1.72 529.5 487.6	

Table I. Direct "diamagnetic" properties. For each compound AB are quoted: $\bar{\chi}^d$, χ^{yy}, $\bar{\sigma}^d$, σ^{yy} in this order.

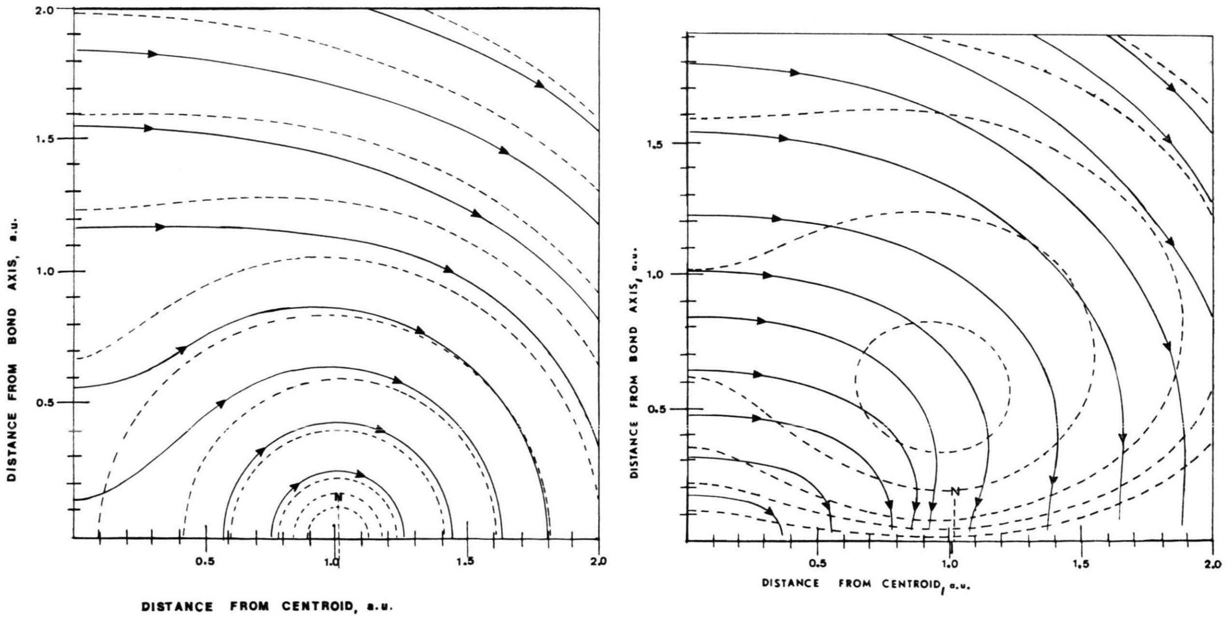

Fig. 3. A: $1\,\sigma_g$ — MO, *f*-function technique.

Fig. 3. B: $1\,\pi_{ux}$ — MO, *f*-function technique.

Fig. 3. Vector maps of induced orbital current densities for the N_2-molecule. The external field is directed perpendicular to the meridian plane shown. Broken lines indicate constant density contours.

A B	H	He	Li	Be	B	C	N	O	F
H	-0.485		-1.30		-1.72		-1.42		-1.11
-0.298^{a}			-1.13		-1.37		-1.32		-0.94
							-1.17^{g}		-0.87^{g}
	-0.49^{b}		-0.96^{c}		$+2.3^{c}$				-1.08^{c}
He									
Li			-4.38						-2.24
-1.87			-4.05						-1.99
									-1.64
			-3.65^{c}						$-1.8^{e,f}$
Be				-4.02					
-1.77				-3.25					
B									-2.57
-1.58									-1.99
									-1.79
									-1.79^{c}
C						-3.20		-2.62	
-1.37						-2.62		-2.14	
						-2.09		-1.72	
								-1.67^{c}	
N							-2.61		
-1.20							-2.11		
							-1.67		
							-1.67^{d}		
O									
-1.12									
F									-2.00
-1.02									-1.75
									-1.17
									-1.35^{c}

[a] Values of the free atoms, from Ref. [16].
[b] Ref. [7].
[c] Values from coupled calculation, Ref. [3].
[d] Experiment, Ref. [4].
[e] Ref. [4].
[f] An experimental value: − 1.27 is quoted in Ref. [19].
[g] From Eq. (16).

Table 2. Mean diamagnetic susceptibilities. Entries for compound AB are results for the cases A, B and C, page 871, together with some reference values. Units are 10^{-10} m^3/mole. For CO, an experimental value of − 1.72 is quoted in: Handbook of Physics and Chemistry, 46th edition, 1965.

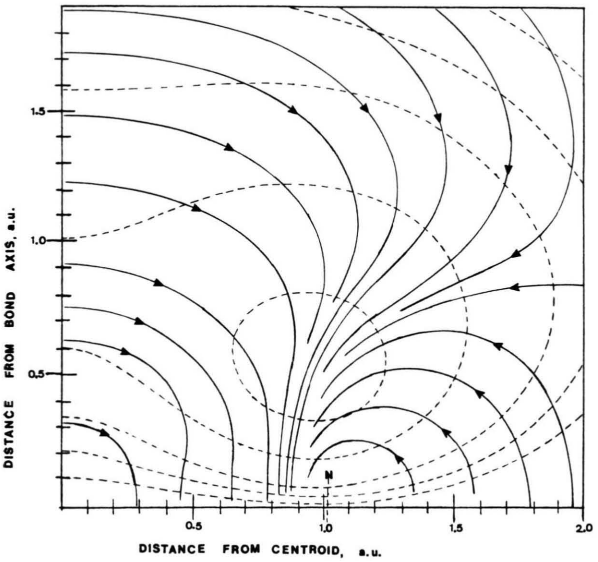

Fig. 3. C: $1\,\pi_{ux}$ — MO, g-function technique.

wavefunction, as $\chi_{\parallel}$ contains no variation contribution. The BLMO functions — much less: all SCF functions — will have a tendency to underestimate the susceptibility as such functions are too concentrated. $\Delta\chi$ is by construction a more sensible quantity than is the mean value; the coincidence in Table 2 is thus seen to be accidental, the true result lying still lower.

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[16] G. Malli and S. Fraga, Theor. Chim. Acta 5, 275 [1966]. — G. Malli and S. Fraga, ibid. 5, 284 [1966].

[17] W. G. Schneider, H. J. Bernstein and J. A. Pople, J. Chem. Phys. 28, 601 [1958].

[18] D. K. Hindermann and C. D. Cornell, J. Chem. Phys 48, 4148 [1968].

[19] J. G. Dorfmann, Diamagnetismus und Chemische Bindung, Verlag Harri Deutsch, Frankfurt/Main und Zürich, 1964.

B \ A	H	He	Li	Be	B	C	N	O	F
H 17.75[a]	27.33		28.43 27.32		31.27 30.82		17.86 17.38		30.17 27.83
He 58.96	26.65[b]		26.5[c]		25[c]				27.9[d]
Li 103.33	100.7 98.63 90.2[c]		103.5 102.5 98.6[c]						102.5 100.8 84.2 87.5[e]
Be 153.81				154.3 150.1					
B 209.44	203.6 193.9 — 263[c]								210.3 196.9 104.5 83[c]
C 269.54						278.3 264.6 69.9		274.6 257.0 9.4 11.5[c]	
N 333.59	329.7 322.4 300.2[g]						345.9 322.9 — 118.9 — 97.8[e]		
O 401.27						413.4 387.4 — 2.1 64.2[c]			
F 472.27	487.9 455.2 424.6[g] 413.7[e]		481.1 455.6 383.3 374.3[e]		482.8 455.4 214.9 250[c]				478.1 456.8 — 52.8 — 232.6[f]

[a] Atomic values, Ref. [16]. [b] Ref. [7]. [c] Coupled calculation, Ref. [3]. [d] Experiment, Ref. [17]. [e] Ref. [4]. [f] Experiment, Ref. [18]. [g] Eq. (16).

Table 3. Mean nuclear magnetic shielding constants at position B for the molecule AB. Entries are results from cases A, B and C, page 871, together with some reference values. Units are ppm.

Pars pro toto we give fuller details for the N_2 molecule. Table 4 shows the MO contributions to the averaged integrated properties fo the π-shell, the Fig. 3 and 4 illustrate the orbital currents for the $1\sigma_g$ MO (by the f-function), the $1\pi_{ux}$ orbital (by the f- and g-function respectively), and the total induced currents according to cases A, B and C above in a qualitative manner. The interesting quantity here is the π_x-orbital, whose node seems to be almost entirely responsible for the antishielding effect, inferred experimentally from molecular beam data[4]. Comparison of Figs 3b and 3c shows the errors induced by the use of the f-function technique, in particular the absence of the ‚paramagnetic' circulation around the nuclei. The general appearance of Fig. 3c is not changed, if in Eq. (17b) the factor V is omitted or set proportional to $(y_a y_b)^2$. The existence of such paramagnetic circulations has been noticed previously for the compound LiH [5a]; we identify their location a posteriori with the position of the node of the 2σ-MO of this molecule. Being far off from the nuclei, they do not influence greatly the shielding constants here.

	$\bar{\chi}^d$ m³/mole	$\bar{\chi}$ m³/mole	$\bar{\sigma}^d$ ppm	$\bar{\sigma}$ ppm
$1\sigma_g$	— 0.226	— 0.014	126.50	117.91
$1\sigma_u$	— 0.226	— 0.014	126.49	117.90
$2\sigma_g$	— 0.364	— 0.356	30.15	16.20
$2\sigma_u$	— 0.841	— 0.327	26.25	17.29
[$1\pi(f)$	— 1.217	— 1.135	48.42	37.82]
$1\pi(g)$		— 0.689		— 403.99
$3\sigma_g$	— 0.762	— 0.226	26.66	15.69
total	— 3.635	— 1.668	384.47	— 118.91
Ref.		— 1.67[a]		— 97.8[a]

[a] cf. Tables 2, 3.

Table 4. Integrated properties. Orbital contributions for N_2.

Figure 5 displays the behaviour of the average integrated properties of the π-shell as a function of the subspace used. This cannot serve to ascertain the convergence of the computation, it indicates

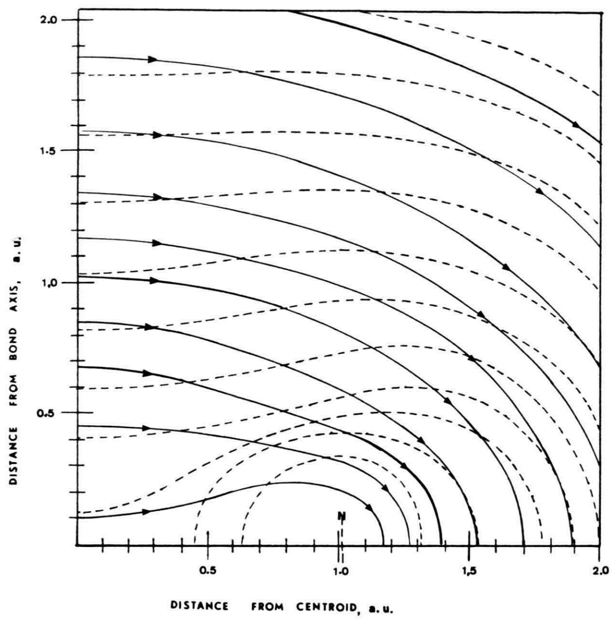

Fig. 4 A

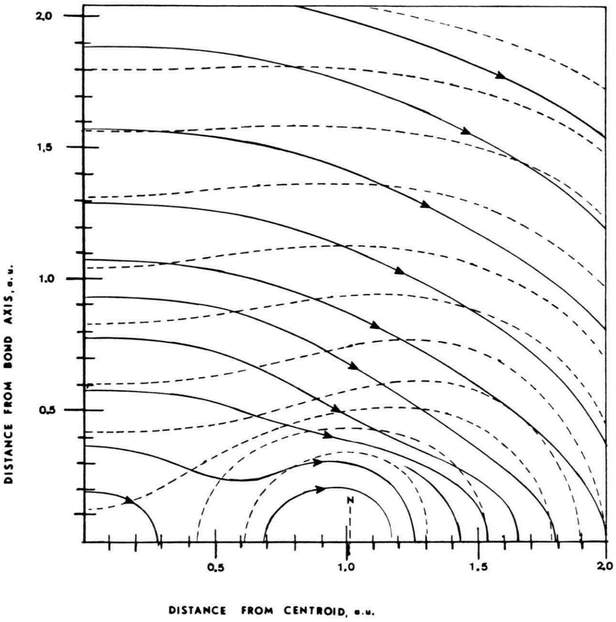

Fig. 4 B

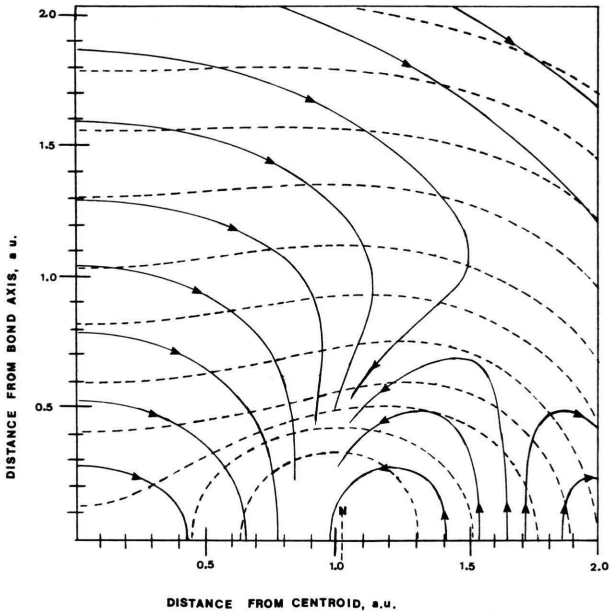

Fig. 4 C

Fig. 4. Vector maps of total induced current densities for N_2 according to cases A, B and C of the text. The external field is directed perpendicular to the meridian plane shown. Broken lines indicate contours of constant densities.

however stability of the functions (17b, c) against the variation of the upper index limits used therein.

The results are obtained for the rigid Born-Oppenheimer molecules described approximately in the SCF scheme via neglect of the second order self-consistency requirement and a somewhat restricted variation for part of the σ-skeleton. We face the usual disappointing situation in Quantum Chemistry that no error estimates can be given. The quantity upon which this calculation is to be judged is the for historical reasons so called high frequency contribution to the susceptibility, the values presented being upper limits in absolute magnitude. The shielding constants follow from the perturbed wavefunctions by a first order calculation and may be in error in either direction. No gauge dependence has been found on examining special cases.

The neglect of self consistency and the use of the local kinetic energy reduces greatly the labor involved in the integration problem, which is one of the reasons of being of the present calculation, providing at the same time a separation into orbital contributions. Computation times for a molecule are typically one minute on an IBM 7090 time scale.

The alterations that couple together the orbital equations are specific to the SCF method; no such terms will appear in more advanced theories. The opinion has been quoted (J. I. Musher) that there is no necessity altogether to perform the more complicated coupled calculations.

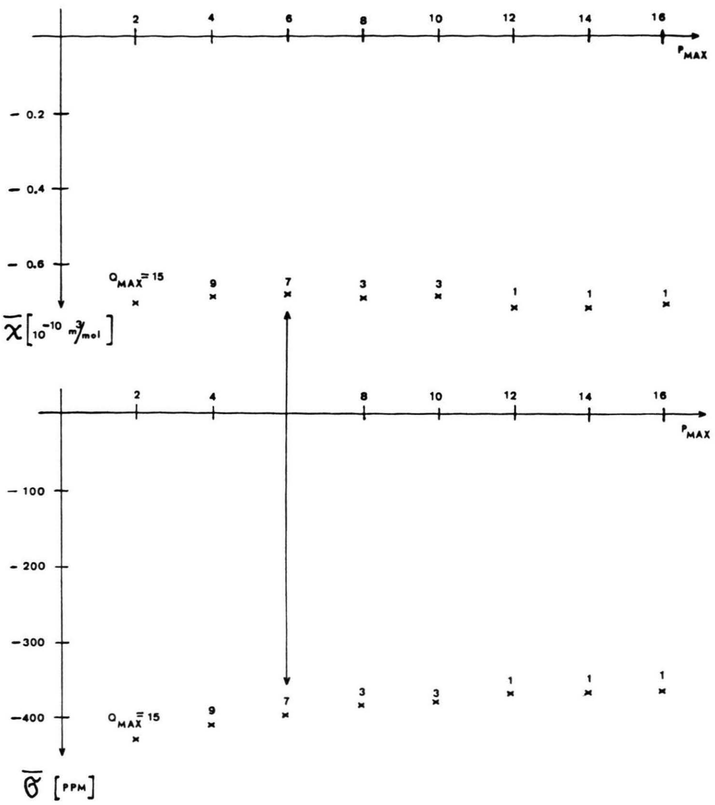

Fig. 5. Integrated properties ($\bar{\sigma}$ and $\bar{\chi}$) for the complete π-shell of the Nitrogen molecule. $Q_{\max}$ and $P_{\max}$ are the upper index limits for the power series, Eq. (17b). The arrow indicates the values chosen.

The main facts about the chemical shifts are apparently incorporated into the uncoupled method, provided we take properly care of the nodes; for fluorine we have found $\delta_F(FH - F_2) = -472.5$ ppm as compared to the experimental value[18] -596.0 ± 2 ppm.

By far the most intriguing point is the discrepancy found for the case of the BH molecule, which here seems to behave like all the other systems studied, but is predicted by coupled calculations[3] to show a positive mean susceptibility and strong antishielding at the Boron site. Errors such as seen for LiH or Li_2 may well be thought of as due to incomplete variation.

The semiclassical treatment of diamagnetic response, for which theory[7] and application have now been given is clearly not capable of explaining the experimental facts. This is not due however to the wrong behaviour of those densities near the nuclei and approaching infinity, but more fundamentally to the incorrect treatment of the kinetic energy, which is the main defect of the Thomas-Fermi theory and its improvements — except possibly in the v. Weizsäcker modification[20].

Relativistic effects are not expected to play an important role here — atomic calculations[21] show at least for light elements no appreciable difference between the Schrödinger and the Dirac treatments.

V. Summary

Several theoretical approaches to the problem of determining the diamagnetic properties of moleculares are shown to be mutually convertible formulations of the steady state condition $\operatorname{div} \boldsymbol{j} = 0$, which in an MO-picture may lead to the uncoupled Hartree-Fock perturbation theory. Calculations have been shown to lead to an acceptable over all description of the diamagnetic properties of first row diatomic molecules. The (uncoupled) procedure

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[21] F. D. Feiock and W. R. Johnson, Phys. Rev. **187**, 39 [1969].

separates the total effects into orbital contributions; the π-MO's have been seen to play a rather particular role.

Owing to some neglects the method is not quantitative in providing a rigorous test of existing wavefunctions; no dependence upon the origin of the vectorpotential subsists in contrast to available coupled calculations.

For principal reasons the semiclassical theory of electronic structure is incapable of explaining correctly the linear magnetic response of nonspherical systems. The formal description is however identical to the quantum-mechanical one.

Most of the time consuming molecular integrals have been held out of the formulation; the computational effort needed is proportional to the number of electrons involved — for given geometry.

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Computational facilities at the Leibniz Rechenzentrum der Bayerischen Akademie der Wissenschaften as well as support from the Deutsche Forschungsgemeinschaft for one of the authors (B.M.L.) are gratefully acknowledged.

Phasengleichgewichte und thermodynamische Analyse des Systems Antimon—Thallium

BRUNO PREDEL und WERNER SCHWERMANN

Institut für Metallforschung der Universität Münster (Westf.)

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Eine Revision der Gleichgewichtsverhältnisse im System Tl—Sb unter Verwendung thermoanalytischer, röntgenographischer und metallographischer Methoden ergab Gleichgewichtsverhältnisse, die von den bisher bekannten merklich abweichen. Es konnte unter anderem eine Verbindung der Zusammensetzung SbTl nachgewiesen und die Existenz von intermetallischen Phasen bei 10 und 25 At.-Proz. Sb erhärtet werden. Die Bestimmung der Schmelzenthalpie ermöglichte die Erschließung der Mischungsenthalpien und Mischungsentropien der β-Thallium-Mischkristalle. Ferner gelang es, die Bildungsenthalpien der intermetallischen Phasen zu ermitteln. Es wurde gezeigt, daß die thermodynamischen Eigenschaften der β-Phase durch einen Umwandlungsanteil dominierend beeinflußt werden, der mit dem Übergang des Antimons von seiner stabilen Modifikation in eine kubisch raumzentrierte Struktur verbunden ist. Es konnte die Umwandlungsenthalpie und Umwandlungsentropie dieser hypothetischen Phasenumwandlung ermittelt werden.

Einführung

Trotz ihrer Bedeutung für die Technik sind bisher nicht alle binären Legierungssysteme mit III- und V-wertigen Komponenten gründlich untersucht worden. Dazu gehört auch das System Antimon—Thallium. In dem von HANSEN und ANDERKO[1] auf Grund früherer Untersuchungen aufgestellten Zustandsdiagramm sind wesentliche Phasengleichgewichte noch weitgehend ungeklärt. Nach den ältesten Untersuchungen von WILLIAMS[2] soll eine unterhalb der eutektischen Temperatur sich bildende intermetallische Verbindung $SbTl_3$ auftreten, wofür EMK-Messungen von KREMANN und LOBINGER[3] jedoch keinen Hinweis lieferten. Indessen deuteten röntgenographische Untersuchungen von BARTH[4] darauf hin, daß $SbTl_3$ ein CsCl-Gitter besitzt und als feste Lösung von Thallium in einer Verbindung TlSb aufzufassen sei. PERSSON und WESTGREN[5] konnten diese Befunde nicht bestätigen. Sie fanden zwei neue Phasen, eine kubisch flächenzentrierte bei etwa 10 At.-Proz. Sb und eine Verbindung Sb_2Tl_7 mit einem komplizierten kubischen Gitter. Röntgen-Untersuchungen von SUGANUMA[6] brachten schließlich eine gewisse Klärung der strukturellen Verhältnisse thalliumreicher Legierungen. Sie bestätigten im wesentlichen die von PERSSON und WESTGREN[5] mitgeteilten Befunde.

Sonderdruckanforderungen an Prof. Dr. B. PREDEL, Institut für Metallforschung, Westfälische Wilhelms-Universität, *D-4400 Münster (Westf.)*, Steinfurter Straße 107.

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