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Physical Properties of Many-Electron Atomic Systems Evaluated from Analytical Hartree-Fock Functions

II. Diamagnetic Susceptibilities*

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Diamagnetic susceptibilities χ_d have been calculated for all positive ions, neutral atoms, and negative ions up to Krypton. It is pointed out that the electrons in the outermost orbitals give the maximum contribution to χ_d.

Die diamagnetische Suszeptibilität χ_d sind für alle positiven Ionen, neutrale Atome und negativen Ionen bis zum Krypton (Z = 36) berechnet worden. Dabei zeigt es sich, daß die äußersten Schalen den größten Beitrag liefern.

Les susceptibilités diamagnetiques χ_d ont été calculées pour tous les ions positives, les atomes neutres et les ions négatives jusqu'au Krypton (Z = 36). On montre que les couches électroniques exterieures donnent la contribution la plus importante.

Theoretical Development

All atomic systems and molecules, regardlees of whether or not they are paramagnetic (i.e., they have permanent magnetic dipoles), show diamagnetic effects. The molar diamagnetic susceptibility is computed from the usual expression given by VAN VLECK [*16*],

$$\chi_d = -\tfrac{1}{6} N \alpha^2 a_0^3 \langle \Phi \mid \sum_i r_i^2 \mid \Phi \rangle , \qquad (1)$$

where N is Avogadro's number, α is the fine structure constant, a_0 the Bohr radius, r_i is the distance of the i-th electron from the nucleus (in a.u.) and Φ is the electronic wave function of the atomic system under consideration. Hence, once the wave functions are available χ_d can be calculated very easily.

SIDWELL and HURST [*12*] have reported the χ_d for some first row atoms and ions, which they evaluated using the analytical Hartree-Fock (HF) functions of ROOTHAAN, SACHS and WEISS [*9*] for He, Li, Be, and Be^+, and ALLEN's [*1*] self-consistent-field (SCF) functions for F, F^-, and Ne.

BANYARD [*2*] calculated the diamagnetic susceptibility of Ne using the HF function of WORSLEY [*17*]. STRAND and BONHAM [*13*] have obtained an approximate analytical expression for the HF potential of neutral atoms by fitting the radial electron density of analytical HF functions; using these expressions they calculated χ_d for all the neutral atoms up to Krypton. More recently SAXENA and NARASIMHAN [*11*] have reported the diamagnetic susceptibilities for all the rare gas atoms using the single-determinant Hartree-Fock-Slater (HFS) functions of HERMAN and SKILLMAN [*6*].

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In a previous paper of this series [*7*], the values of the nuclear magnetic shielding constants σ for a large number of atomic systems were reported. In this paper the values of the diamagnetic susceptibilities of neutral atoms (up to $Z = 36$, and also Z = 42, 54) and their positive and negative ions (up to $Z = 36$) are presented. These values have been calculated using the HF functions of Clementi [*4*], Malli and Roothaan [*8*], Roothaan and Synek [*10*], Synek [*14*], and Synek and Stungis [*15*].

Results and Discussion

Tab. 1 presents the diamagnetic susceptibilities of all the neutral atoms up to Z = 36, and also for Z = 42, 54; this table also includes, for comparison, the results of previous workers.

Our results agree to within 0.5% with the values calculated by Strand and Bonham [*13*] for neutral atoms, up to Z = 10. This implies that the analytical fit to the HF potential achieved by Strand and Bonham using only a few parameters is excellent for these light atoms. However, it can be seen that this fit is not so

Table 1. *Diamagnetic susceptibilities* ($\chi_a \cdot 10^6$) *for the groundstates of neutral atoms* (*in* $\mathrm{cm}^3 \cdot \mathrm{mole}^{-1}$)

Z	This Calculation[a]	Other Calculation[b]	Z	This Calculation[a]	Other Calculation[b]
2	1.878	1.9	21	42.126	48.0
3	14.764	15.2	22	39.760	44.0
4	13.724	14.1	23	37.671	41.0
5	12.556	12.7	24	30.113	38.0
6	10.930	11.0	25	34.135	36.0
7	9.565	9.6	26	32.593	34.0
8	8.846	8.9	27	31.221	32.0
9	8.110	8.1	28	29.982	30.0
10	7.429	7.4[c]	29	26.304	28.0
11	21.500	18.1	30	27.687	27.0
12	23.451	22.2	31	32.421	31.0
13	26.518	24.6	32	32.946	33.0
14	25.559	24.9	33	32.529	34.0
15	23.985	24.2	34	32.586	34.0
16	23.110	23.2	35	32.095	34.0
17	21.894	22.1	36	31.315	33.0[e]
18	20.626	20.9[d]	42	44.770	
19	40.569	52.0	54	44.846	43.93[f, g]
20	44.833	53.0			

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[a] Evaluated using the HF functions of Clementi [4], Malli and Roothaan [8], Roothaan and Synek [*10*], Synek [*14*],and Synek and Stungis [*15*].

[b] Evaluated by Strand and Bonham [*13*], except for Z = 54.

[c] Sidwell and Hurst [*12*] give a value of 7.475, Saxena and Narasimham [*11*] a value of 7.09, and Banyard [*2*] a value of 5.8.

[d] Saxena and Narasimhan [*11*] give a value of 19.17.

[e] Saxena and Narasimhan [*11*] report a value of 29.06.

[f] Reported by Saxena and Narasimhan [*11*].

[g] The experimental value of 45.54 ± 0.70 was reported by Barter, Meisenheimer and Stevenson [*3*].

Table 2. *Diamagnetic susceptibilities* ($\chi_d \cdot 10^6$) *for groundstates* (*in* cm$^3 \cdot$mole^{-1})

Z	positive ions[a]	negative ions[b]	Z	positive ions[a]	negative ions[b]	Z	positive ions[a]	negative ions[b]
3	0.706	69.673	15	16.605	38.568	26	15.940	69.894
4	5.203		16	16.487	34.049	27	15.471	65.755
5	6.299	31.529	17	16.392	30.335	28	15.133	38.517
6	6.388	20.830	18	16.034		29	14.673	60.104
7	6.138	17.665	19	15.472	126.428	30	17.901	
8	5.802	14.845	20	24.761		31	19.998	66.418
9	5.604	12.638	21	18.157	88.196	32	22.876	51.296
10	5.352		22	17.646	86.203	33	24.184	48.524
11	5.078	78.271	23	17.147	82.273	34	24.730	45.331
12	11.208		24	16.496	78.606	35	25.269	42.204
13	13.822	58.777	25	16.320	73.154	36	25.374	
14	16.042	43.165				42	29.744	

[a] Evaluated using the HF functions of CLEMENTI [*4*] and ROOTHAAN and SYNEK [*10*].

[b] Evaluated using the HF functions of CLEMENTI [*4*].

satisfactory for heavier atoms. For atoms from Z = 11 to $Z = 18$ their results differ from ours by as much as 14%, for Z = 11, the difference decreasing gradually until it is only 1.5% for $Z = 18$. At Z = 19 the maximum difference is observed, i.e., 33%. The difference decreases from that point on until it is only of 2.5% for Z = 30. At Z = 31 there is once more an increase in the disagreement (4.5%), and this difference remains constant up to Z = 36.

Table 3. *Partial contributions* (%) *to* χ_d *from the various shells in Xenon*

Shell	Electronic Population[a] (%)	Contribution (%) to χ_d
$1s$	3.7	0.0038
$2s$	3.7	0.065
$3s$	3.7	0.427
$4s$	3.7	2.240
$5s$	3.7	15.040
$2p$	11.1	0.136
$3p$	11.1	1.176
$4p$	11.1	7.134
$5p$	11.1	58.470
$3d$	18.55	1.589
$4d$	18.55	13.712

[a] Referred to the total number of electrons in the atom.

For Z = 54 the value of χ_d calculated by SAXENA and NARASIMHAM [*11*] differs from ours by only 2%, our value agreeing perfectly with the experimental value of BARTER, MEISENHEIMER and STEVENSON [*3*] within the limits of the experimental uncertainty. As SAXENA and NARASIMHAN [*11*] used the HFS functions for rare gases, it appears that those functions give an accurate description of the outermost orbitals, because these orbitals make the largest contribution to χ_d.

Tab. 2 collects the χ_d for the positive and negative ions for atoms up to Z = 36. The partial contributions of the different electronic shells to χ_d are analyzed in Tab. 3, which collects the results for Xe. It can be seen that the largest contributions come from the shells $5p$ and $5s$, the former being the most important. These are the two outermost shells, and by contrast it can be seen that the innermost shells make the smallest contributions.

These results are very satisfactory from the following point of view. The predominant importance of the outer shells implies that when calculating the

Table 4. *Diamagnetic susceptibilities* ($\chi_a \cdot 10^6$) *for some excited states of neutral atoms*[a] (*in* cm^3·mole^{-1})

Atom	State		Atom	State	
He[b]	^1S	18.156	P	^2P	25.190
	^3S	20.358	S	^1D	23.398
C	^1D	11.354		^1S	23.925
	^1S	12.153	Cr	^5D	35.827
N	^2D	9.918	Cu	^2D	28.781
	^2P	10.175	Ge	^1D	33.911
O	^1D	9.008	As	^2D	33.304
	^1S	9.264		^2P	33.895
Si	^1D	26.404	Se	^1D	32.969
	^1S	28.028		^1S	33.574
P	^2D	24.676			

[a] Evaluated using the HF functions of Clementi [*4*] and Malli and Roothaan [*8*].

[b] These excited states correspond to the electronic configuration (1*s*) (2*s*), as determined by Fraga and Birss [*5*].

diamagnetic susceptibility for heavier atoms there is no need to include the relativistic effects, which are dominant in the inner shells. But it must be emphasised that the functions to be used for such calculations must provide a fairly accurate description of the outer shells. As the experimental value for χ_d for Xe is in excellent agreement with the theoretically predicted value calculated in this paper using HF functions, one can conclude that these functions describe adequately the electronic density at large distances from the nucleus.

In paper I of this series [7] it was noticed that the inner shells give the most important contribution to the nuclear magnetic shielding constants σ; and as most of the wave functions used satisfied the cusp condition exactly, it means that they are very accurate near the nucleus. Therefore the wave functions used in this series of calculations provide a very satisfactory description of the electronic density near the nucleus as well as at large distances from it.

Tab. 4, 5, and 6 present the χ_d values for some excited states of neutral atoms, positive and negative ions, with the same electronic configurations as the corresponding groundstates presented in Tab. 1, and 2. The only exception is that of

Table 5. *Diamagnetic susceptibilities* ($\chi_a \cdot 10^6$) *for some excited states of positive ions*[a] (*in* cm^3·mole^{-1})

Atom	State		Atom	State	
N	^1D	6.267	S	^2P	16.913
	^1S	6.490	Cl	^1D	16.512
O	^3P	6.026		^1S	16.701
	^2D	5.932	As	^1D	24.499
F	^1D	5.666		^1S	25.034
	^1S	5.767	Se	^2D	25.055
P	^1D	16.883		^2P	25.289
	^1S	17.838	Br	^1D	25.439
S	^2D	16.762		^1S	25.710

[a] Calculated using the HF functions of Clementi [*4*].

Table 6. *Diamagnetic susceptibilities* ($\chi_d \cdot 10^6$) *for some excited states of negative ions*[a] (*in* $\mathrm{cm}^3 \cdot \mathrm{mole}^{-1}$)

Atom	State		Atom	State	
B	^1D	40.898	Si	^2P	51.353
	^1S	29.126	P	^1D	40.173
C	^2D	23.315		^1S	42.103
	^2P	25.481	Ga	^1D	79.381
N	^1D	18.511	Ge	^2D	55.622
	^1S	19.992		^2P	59.792
Al	^1D	73.830	As	^1D	50.216
	^1S	122.187		^1S	52.161
Si	^2D	47.449			

[a] Evaluated using the HF functions of Clementi [*4*].

the $^{1,3}S$ excited states of He, with the configuration $(1s)\,(2s)$, determined by Fraga and Birss [*5*].

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