PHYSICAL REVIEW A VOLUME 2, NUMBER 4 OCTOBER 1970

# Hartree-Fock Diamagnetic Susceptibilties*

Lawrence B. Mendelsohn[†] and Frank Biggs
*Sandia Laboratories, Albuquerque, New Mexico* 87115

and

Joseph B. Mann
*University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico* 87544

(Received 30 March 1970)

The diamagnetic susceptibilities of all free atoms up to $Z = 103$ are calculated within the nonrelativistic and relativistic numerical Hartree-Fock approximations. Relativistic calculations are also performed for certain ions. The use of Dirac self-consistent wave functions leads to lower calculated susceptibilities. This effect becomes appreciable at very large atomic numbers; e.g., in uranium a decrease of 12.3% below the nonrelativistic value is found. For the case of the rare gases, the Hartree-Fock diamagnetic susceptibilities are found to lie above the experimental values. This is attributed to the omitted effects of electron correlation. For the noble and divalent metals, the calculated atomic-core diamagnetic susceptibilities lie above the experimental metallic values, since we have not included the paramagnetism of the conduction electrons.

## I. INTRODUCTION

Accurate values of the diamagnetic susceptibilities of free atoms and ions can be utilized to obtain the elastic-scattering cross section of fast electrons from atoms at zero scattering angle[1] and x-ray coherent atomic scattering factors for small momentum transfers.[2,3] In addition, free-ionic (core) diamagnetic susceptibilities are of importance in analyzing susceptibility measurements in metals and semiconductors.[4] From these measurements, properties of the conduction electrons, e.g., effective mass, can be obtained.

Atomic diamagnetic susceptibilities using various nonrelativistic approximate screened wave functions have previously been calculated and compared.[5] It was concluded that the minimal-basis Slater-type-orbital analytic self-consistent-field wave functions of Clementi *et al.*[6,7] give the best agreement with experiment over the range considered (up to $Z = 86$). However, such a minimal basis set may lead to diamagnetic susceptibilities which are greatly in error when compared to those obtained by using either nonrelativistic large-basis-set analytic calculations or numerical Hartree-Fock calculations. This is observed in Table I where we compare the calculated susceptibilities of the rare gases using more accurate wave functions with those obtained using the minimal-basis-set wave functions. Large differences are observed.

We summarize the state of the art for the calculation of diamagnetic susceptibilities of atoms by listing in Table I the results of various calculations for the rare gases. Two sets of approximations to the nonrelativistic Hartree-Fock theory by Clementi *et al.*[6,7] are given in columns 3 and 4. Hartree-Fock results of Malli and Froese[8] are given in column 5, and our present Hartree-Fock results in column 6. Relativistic Hartree-Fock-Slater results of Feiock and Johnson[9] are in column 7, and our present relativistic Hartree-Fock results are in column 8.

In addition to these numbers, we mention that Goddard,[10] using a 12-term-basis analytical Hartree-Fock calculation, obtains a value of 1.877 for helium, and Pekeris,[11] in an "exact" nonrelativistic calculation, obtains a value of 1.890.

Malli and Froese[8] report results for atomic numbers up to $Z = 86$. They did not, however, consider configurations with more than one open shell. Therefore, for some elements they used an atomic configuration different from the true ground-state configuration. The agreement between our numbers and theirs is about the same as that for the rare gases shown in Table I whenever the configurations agree. For about 20% of the elements with $Z \leqslant 86$ we use different atomic configurations; consequently, these results differ markedly.

Feiock and Johnson[9] consider only closed-shell atoms and ions. In obtaining the results given in column 7 of Table I, they calculated relativistic Hartree-Fock-Slater wave functions and utilized a relativistic form for the diamagnetic-susceptibility operator. They also performed the relativistic calculations using the Van Vleck form of the diamagnetic susceptibility and found very close agreement between the two calculations. All other

TABLE I. Comparison of theoretical results for rare-gas diamagnetic susceptibilities ($-\chi$ in units of $10^{-6}$ cm$^3$/mole).

| Element | $Z$ | Clementi's $\xi$ | Clementi's $\xi'$ | Malli-Froese HF | Present work HF | Feiock-Johnson RHFS | Present work RHF |
|---|---|---|---|---|---|---|---|
| He | 2 | 1.665 | 1.664 | 1.878 | 1.8767 | 1.882 | 1.8766 |
| Ne | 10 | 5.770 | 5.863 | 7.426 | 7.4224 | 7.101 | 7.4167 |
| A | 18 | 17.421 | 18.257 | 20.628 | 20.6189 | 19.16 | 20.5706 |
| Kr | 36 | 26.751 | 27.887 | 31.321 | 31.3073 | 28.81 | 30.9705 |
| Xe | 54 | 42.623 | 38.942 | 49.641 | 49.6191 | 45.00 | 48.4686 |
| Rn | 86 | 55.719 | 59.332 | 64.368 | 64.3409 | 56.44 | 60.5823 |

entries in the table, including our relativistic calculations, utilized the Van Vleck form of the diamagnetic-susceptibility operator. The differences between our relativistic results and theirs for closed-shell ions are typical of the differences cited for the rare-gas atoms. Except for helium, their results lie below ours. This is consistent with the work of Cowan *et al.*,[12] where it was shown that the use of the Slater approximation for exchange in nonrelativistic Hartree-Fock calculations leads to an electron density which is smaller at larger radii than the corresponding density obtained without making this approximation.

In the present work we have calculated the numerical Hartree-Fock diamagnetic susceptibilities, both nonrelativistically and relativistically, of all neutral free atoms up to $Z = 103$ and of some of the important ions, using the individual orbital data obtained from the calculations of one of us.[13,14] In this way we have treated exchange exactly and have not restricted our calculations to closed-shell or one-open-shell configurations. For free atoms with $Z = 95$, 96, and 97, two alternate ground-state configurations were considered. For the relativistic calculations, the Dirac wave functions utilized were obtained in a self-consistent manner, with complete exchange as originally derived by Grant.[15] The nucleus was taken to be finite. The Breit magnetic-interaction term was not used in obtaining the relativistic wave functions. For the nonrelativistic and relativistic calculations, the open shells were handled in the manner described by Slater.[16]

## II. DISCUSSION OF RESULTS

The ground-state atomic configurations used in the calculations are given in abbreviated form in Table II. Only the configuration of the outer electrons is specified. For purposes of comparison, we include the experimental results quoted by Dehn and Mulay,[5] except for Ge[17] and In,[18] where we have substituted what we believe to be more accurate experimental values. For the case of the rare gases, we quote the latest experimental results of Barter *et al.*[19] in addition to the Dehn and Mulay values. The Barter measurements are quoted after those of Dehn and Mulay and are separated from them by a semicolon. In converting our calculated results, we have used

$$-\chi = 0.791\,987\times 10^{-6}\langle \textstyle\sum_i r_i^2\rangle_{\mathrm{av}}\ \mathrm{cm}^3/\mathrm{mole}\,, \qquad (1)$$

where $r_i^2$ is expressed in atomic units. The values of Avogadro's number, the fine structure constant, and the Bohr radius used to obtain the constant in Eq. (1) are taken from the 50th edition of the *Handbook of Chemistry and Physics*. In order to make a comparison between theory and experiment for the noble metals Cu, Ag, and Au and the divalent metals Zn, Cd, and Hg, we have calculated the free ions making up the atomic cores for these metals. The calculated diamagnetic susceptibilities for these ions all lie above the experimental values for the metals and are compared on the same line of the table. The difference can be largely attributed to the paramagnetism of the conduction electrons. We have also calculated free-ion diamagnetic susceptibilities for Si(+4), Ga(+3), Ge(+4), In(+3), Sn(+4), Tl(+3), and Pb(+4). For Ge and Pb, the ion calculations agree well with the experimental values. However, in general, for these solids it is difficult to correlate theory and experiment because of the more complicated electron behavior, the effects of paramagnetic impurities, anisotropy, etc. The same is true of the experimental results for liquids, and these are included only for purposes of completeness. The number of significant places appearing in our results indicates the computational accuracy achieved with the theoretical models we have used to calculate the diamagnetic susceptibilities.

In comparing the relativistic and nonrelativistic diamagnetic susceptibilities, we note that the effect of including relativity is to pull in the electron charge distribution, the spatial contraction becoming much larger for very large $Z$. Thus, for

TABLE II. Calculated and experimental diamagnetic susceptibilities ($-\chi$ in units of $10^{-6}$ cm$^3$/mole).[a]

| Atomic number | Element | Configuration identification | Hartree-Fock Nonrelativistic | Hartree-Fock Relativistic | Experimental[b] |
|---|---|---|---|---|---|
| 1 | H | $1s$ | 2.3760 | 2.3759 | |
| 2 | He | $1s^2$ | 1.8767 | 1.8766 | 1.88(g); 2.02±0.08 |
| 3 | Li | $2s$ | 14.7563 | 14.7539 | |
| 4 | Be | $2s^2$ | 13.7162 | 13.7117 | 9.0 |
| 5 | B | $2p$ | 12.5538 | 12.5487 | 6.70 |
| 6 | C | $2p^2$ | 11.1271 | 11.2664 | 6.00 |
| 7 | N | $2p^3$ | 9.9163 | 9.9541 | 6.00(g) |
| 8 | O | $2p^4$ | 8.9234 | 8.9272 | |
| 9 | F | $2p^5$ | 8.1052 | 8.0995 | |
| 10 | Ne | $2p^6$ | 7.4224 | 7.4167 | 6.74(g); 6.96±0.14 |
| 11 | Na | $3s$ | 21.5070 | 21.4595 | |
| 12 | Mg | $3s^2$ | 23.4420 | 23.3885 | |
| 13 | Al | $3p$ | 26.5130 | 26.4448 | |
| 14 | Si | $3s^23p^2$ | 25.9578 | 26.1706 | |
| | Si(+4) | $2p^6$ | | 2.2857 | 3.90 |
| 15 | P | $3p^3$ | 24.6674 | 24.6901 | 20.8, 26.6 |
| 16 | S | $3p^4$ | 23.2514 | 23.2151 | 15.5(α), 14.9(β), 15.4(l) |
| 17 | Cl | $3p^5$ | 21.8848 | 21.8344 | 20.25(g) |
| 18 | Ar | $3p^6$ | 20.6189 | 20.5706 | 19.6(g); 19.32 |
| 19 | K | $4s$ | 40.5747 | 40.3473 | |
| 20 | Ca | $4s^2$ | 44.7994 | 44.5121 | |
| 21 | Sc | $3d4s^2$ | 42.1058 | 41.8101 | |
| 22 | Ti | $3d^24s^2$ | 39.7263 | 39.4127 | |
| 23 | V | $3d^34s^2$ | 37.6261 | 37.2951 | |
| 24 | Cr | $3d^54s$ | 31.5656 | 31.3107 | |
| 25 | Mn | $3d^54s^2$ | 34.0785 | 33.7121 | |
| 26 | Fe | $3d^64s^2$ | 32.5623 | 32.1757 | |
| 27 | Co | $3d^74s^2$ | 31.1840 | 30.7768 | |
| 28 | Ni | $3d^84s^2$ | 29.9245 | 29.4967 | |
| 29 | Cu | $3d^{10}4s$ | 25.4777 | 25.1478 | |
| | Cu(+1) | $3d^{10}$ | | 14.8509 | 5.46(s), 6.16(l) |
| 30 | Zn | $3d^{10}4s^2$ | 27.7030 | 27.2337 | |
| | Zn(+2) | $3d^{10}$ | | 11.6686 | 11.4(s), 7.8(l) |
| 31 | Ga | $4s^24p$ | 32.4540 | 31.9178 | |
| | Ga(+3) | $3d^{10}$ | | 9.7039 | 21.6 |
| 32 | Ge | $4s^24p^2$ | 33.4018 | 33.1294 | |
| | Ge(+4) | $3d^{10}$ | | 8.2946 | 8.0 |
| 33 | As | $4p^3$ | 33.3064 | 32.9293 | 5.5(α), 23.7(β), 23.0(γ) |
| 34 | Se | $4p^4$ | 32.7922 | 32.4067 | 25.00 |
| 35 | Br | $4p^5$ | 32.0910 | 31.7261 | 36.7(g), 56.4(l) |
| 36 | Kr | $4p^6$ | 31.3073 | 30.9705 | 28.8(g); 29.0±0.4 |
| 37 | Rb | $5s$ | 54.0493 | 52.9025 | |
| 38 | Sr | $5s^2$ | 60.2404 | 58.8619 | |
| 39 | Y | $4d5s^2$ | 58.1241 | 56.8798 | |
| 40 | Zr | $4d^25s^2$ | 55.8727 | 54.5983 | |
| 41 | Nb | $4d^45s$ | 48.8166 | 47.9251 | |
| 41 | Mo | $4d^55s$ | 46.9921 | 46.1021 | |
| 43 | Tc | $4d^55s^2$ | 50.0972 | 48.7138 | |
| 44 | Ru | $4d^75s$ | 43.8654 | 42.8890 | |
| 45 | Rh | $4d^85s$ | 42.4997 | 41.4701 | |
| 46 | Pd | $4d^{10}$ | 33.7549 | 34.0409 | |
| 47 | Ag | $4d^{10}5s$ | 40.0681 | 38.9317 | |
| | Ag(+1) | $4d^{10}$ | | 27.2404 | 19.5(s), 24.0(l) |
| 48 | Cd | $4d^{10}5s^2$ | 43.0532 | 41.4619 | |
| | Cd(+2) | $4d^{10}$ | | 23.0768 | 19.8(s), 18.0(l) |
| 49 | In | $5s^25p$ | 48.7106 | 46.8509 | |
| | In(+3) | $4d^{10}$ | | 20.1089 | 10.3(s) |
| 50 | Sn | $5s^25p^2$ | 50.4322 | 48.7687 | |
| | Sn(+4) | $4d^{10}$ | | 17.8307 | 37.0(gray), 4.5(l) |

TABLE II. (*continued*).

| Atomic number | Element | Configuration identification | Hartree-Fock Nonrelativistic | Hartree-Fock Relativistic | Experimental[b] |
|---|---|---|---|---|---|
| 51 | Sb | $5p^3$ | 50.8709 | 49.3531 | 99(s), 2.5(l) |
| 52 | Te | $5p^4$ | 50.7190 | 49.3442 | 39.5(s), 6.4(l) |
| 53 | I | $5p^5$ | 50.2561 | 49.0040 | 88.7($I_2$, s) |
| 54 | Xe | $5p^6$ | 49.6191 | 48.4686 | 43.9(g); 45.5 ± 0.7 |
| 55 | Cs | $6s$ | 77.5201 | 74.1341 | |
| 56 | Ba | $6s^2$ | 86.0378 | 82.0276 | |
| 57 | La | $5d$ | 83.6910 | 79.9453 | |
| 58 | Ce | $4f5d$ | 81.9014 | 78.0290 | |
| 59 | Pr | $4f^3$ | 80.5657 | 76.2710 | |
| 60 | Nd | $4f^4$ | 78.9522 | 74.5600 | |
| 61 | Pm | $4f^5$ | 77.4217 | 72.9319 | |
| 62 | Sm | $4f^6$ | 75.9655 | 71.3776 | |
| 63 | Eu | $4f^7$ | 74.5766 | 69.8805 | |
| 64 | Gd | $4f^7 5d$ | 73.0128 | 68.5458 | |
| 65 | Tb | $4f^8 5d$ | 71.7646 | 67.2322 | |
| 66 | Dy | $4f^{10}$ | 70.7586 | 65.7364 | |
| 67 | Ho | $4f^{11}$ | 69.5875 | 64.4562 | |
| 68 | Er | $4f^{12}$ | 68.4617 | 63.2204 | |
| 69 | Tm | $4f^{13}$ | 67.3774 | 62.0260 | |
| 70 | Yb | $4f^{14}$ | 66.3324 | 60.8704 | |
| 71 | Lu | $4f^{14} 5d$ | 65.2812 | 60.5511 | |
| 72 | Hf | $5d^2$ | 63.8922 | 59.1646 | |
| 73 | Ta | $5d^3$ | 62.5007 | 57.7222 | |
| 74 | W | $5d^4$ | 61.1599 | 56.3161 | |
| 75 | Re | $5d^5$ | 59.8812 | 55.0627 | |
| 76 | Os | $5d^6$ | 58.6648 | 53.8209 | |
| 77 | Ir | $5d^7$ | 57.5075 | 52.6134 | |
| 78 | Pt | $5d^9 6s$ | 51.8899 | 48.5488 | |
| 79 | Au | $5d^{10} 6s$ | 50.9365 | 47.4836 | |
| | Au(+1) | $5d^{10}$ | | 37.6089 | 28.0(s), 34.0(l) |
| 80 | Hg | $5d^{10} 6s^2$ | 54.3522 | 49.2436 | 78.3(g) |
| | Hg(+2) | $5d^{10}$ | | 32.8769 | 24.1(s), 33.4(l) |
| 81 | Tl | $6s^2 6p$ | 60.8168 | 54.3681 | |
| | Tl(+3) | $5d^{10}$ | | 29.4359 | 50.90 |
| 82 | Pb | $6s^2 6p^2$ | 63.2501 | 56.5742 | |
| | Pb(+4) | $5d^{10}$ | | 26.7428 | 23.00 |
| 83 | Bi | $6p^3$ | 64.2862 | 58.9161 | 280.1(s), 10.5(l) |
| 84 | Po | $6p^4$ | 64.6399 | 60.0243 | |
| 85 | At | $6p^5$ | 64.6083 | 60.4926 | |
| 86 | Rn | $6p^6$ | 64.3409 | 60.5823 | |
| 87 | Fr | $7s$ | 95.0350 | 84.0324 | |
| 88 | Ra | $7s^2$ | 105.2005 | 92.3171 | |
| 89 | Ac | $6d$ | 103.2580 | 91.9727 | |
| 90 | Th | $6d^2$ | 101.1773 | 90.3145 | |
| 91 | Pa | $5f^2 6d$ | 99.6607 | 87.8586 | |
| 92 | U | $5f^3 6d$ | 98.0075 | 85.9921 | |
| 93 | Np | $5f^4 6d$ | 96.4357 | 84.2273 | |
| 94 | Pu | $5f^6$ | 95.0166 | 81.6786 | |
| 95 | Am | $5f^6 6d$ | | 80.9466 | |
| | Am | $5f^7$ | 93.5852 | 80.1014 | |
| 96 | Cm | $5f^7 6d$ | 92.1321 | 79.5182 | |
| | Cm | $5f^8$ | | 78.5620 | |
| 97 | Bk | $5f^8 6d$ | 90.8151 | 78.1524 | |
| | Bk | $5f^9$ | 90.8941 | 77.0665 | |
| 98 | Cf | $5f^{10}$ | 89.6260 | 75.6145 | |
| 99 | Es | $5f^{11}$ | 88.4042 | 74.2037 | |
| 100 | Fm | $5f^{12}$ | 87.2261 | 72.8308 | |
| 101 | Md | $5f^{13}$ | 86.0887 | 71.4947 | |
| 102 | No | $5f^{14}$ | 84.9893 | 70.1920 | |
| 103 | Lw | $5f^{14} 6d$ | 83.8783 | 71.3771 | |

[a] The letters g, l, and s signify gas, liquid, and solid, respectively; $\alpha$, $\beta$, and $\gamma$ signify solid phases.

[b] The experimental results are from Ref. 5, with the exception of the second set of rare-gas results which are from Ref. 19 and the Ge and In results which are from Refs. 17 and 18, respectively.

uranium ($Z=92$), use of Dirac wave functions leads to a decrease of 12.3% in the calculated diamagnetic susceptibility. At $Z=54$ (xenon), relativistic effects account only for a 2.3% reduction in the calculated diamagnetic susceptibility.

In the case of the rare gases where experiments have been carried out many times with free atoms,[20-23] it appears that nonrelativistic Hartree-Fock results for the diamagnetic susceptibilities are consistently larger than the experimental values and do not fall within the error bars quoted by Barter. Including relativistic effects does not alter this conclusion, although it does bring theory and experiment for xenon into slightly better agreement. We note that the above observation is diametrically opposed to that obtained by examining the results of the nonrelativistic minimal-basis Hartree-Fock calculations,[5] where the susceptibilities for the rare gases consistently fall below the experimental values. Dawson[24] has found that the use of configuration-interaction wave functions which include electron correlation leads to charge distributions which are less extensive radially than those of the Hartree-Fock model. Therefore, we expect that calculations of diamagnetic susceptibilities in which wave functions more accurate than those of the Hartree-Fock model are used will be smaller than the Hartree-Fock results and in better agreement with the rare-gas experimental results. The relativistic Hartree-Fock-Slater results of Feiock and Johnson[9] do fall within the error bars quoted by Barter for the rare gases except for helium. As noted before, the effect of using the Slater exchange approximation is to lower the electron density far from the nucleus. It appears that for the calculation of $r^2$ in the rare-gas atoms up to xenon, this added approximation compensates greatly for the omitted effects of electron-electron correlation.

In Table II, the experimental atomic results quoted for Hg, Br, and Cl are obtained by taking one-half the value measured for the diatomic gases. Outside of Cl, it would appear that taking two times the theoretical atomic value to estimate the diamagnetic susceptibility for the diatomic molecule greatly underestimates the experimental results. We would expect that an extension of the susceptibility calculation method of De La Vega and Hameka[25] using LCAO-MO-SCF wave functions should lead to improved agreement between theory and experiment for diatomic gases.

## ACKNOWLEDGMENTS

We wish to thank E. J. McGuire and T. A. Green of Sandia Laboratories for helpful discussions.

---

[*] Work supported by the U. S. Atomic Energy Commission.

[†] Permanent address: Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn, N. Y. 11201.

[1] J. A. Ibers, Acta Cryst. 11, 178 (1968).

[2] D. R. Chipman and L. D. Jennings, Phys. Rev. 132, 728 (1963).

[3] L. B. Mendelsohn (unpublished).

[4] D. K. Stevens *et al.*, Phys. Rev. 100, 1084 (1955).

[5] J. T. Dehn and L. N. Mulay, J. Chem. Phys. 48, 4910 (1968).

[6] E. Clementi and D. L. Raimondi, J. Chem. Phys. 38, 2686 (1963).

[7] E. Clementi, D. L. Raimondi, and W. P. Reinhardt, J. Chem. Phys. 47, 1300 (1967).

[8] G. Malli and C. Froese, Intern. J. Quantum Chem. IS, 99 (1967).

[9] F. D. Feiock and W. R. Johnson, Phys. Rev. 187, 39 (1969).

[10] W. A. Goddard, J. Chem. Phys. 48, 1008 (1968).

[11] C. L. Pekeris, Phys. Rev. 115, 1216 (1959).

[12] R. D. Cowan, A. C. Larson, D. Liberman, J. B. Mann, and J. Waber, Phys. Rev. 144, 5 (1967).

[13] J. B. Mann, LASL Report No. 3691, 1968 (unpublished).

[14] J. B. Mann (unpublished).

[15] I. P. Grant, Proc. Roy. Soc. (London) A262, 555 (1961).

[16] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Chaps. 13 and 17.

[17] R. Bowers, Phys. Rev. 108, 683 (1957).

[18] G. Busch and S. Yuan, Physik Kondensierten Materie 1, 37 (1963).

[19] C. Barter *et al.*, J. Phys. Chem. 64, 1312 (1960).

[20] A. P. Wills and L. G. Hector, Phys. Rev. 23, 209 (1924).

[21] G. G. Havens, Phys. Rev. 43, 992 (1933).

[22] K. E. Mann, Z. Physik 98, 548 (1936).

[23] L. Abonnenc, Compt. Rend. 208, 986 (1939).

[24] B. Dawson, Acta Cryst. 14, 1117 (1961).

[25] J. R. De La Vega and H. F. Hameka, Physica 35, 313 (1967).