Theoret. chim. Acta (Berl.) 6, 278—280 (1966)

Relatio

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

IV. Fermi Contact Interaction Term*

GULZARI MALLI and SERAFIN FRAGA

Division of Theoretical Chemistry, Department of Chemistry
University of Alberta, Edmonton, Alberta

Received June 20, 1966

A particle with spin has an associated magnetic moment vector parallel to the spin vector. In particular, for an electron and a nucleus one can write, respectively, $\mu_e = g_e \mu_B \boldsymbol{s}$, $\mu_I = g_n \mu_N \boldsymbol{I}$, where g_e and g_n are the electronic and nuclear gyromagnetic ratios, μ_B and μ_N are the Bohr and nuclear magnetons, and $\boldsymbol{s}$ and $\boldsymbol{I}$ are the respective spin vectors (corresponding to the electron and nuclear spin quantum numbers, s and I).

FERMI [2, 3] has shown that the interaction between the magnetic moment of an electron and the magnetic moment of a nucleus leads to a term in the hyperfine structure splitting of the atomic energy levels. This interaction term is called the Fermi contact term because it is effective only at extremely short ranges. As only the s-type orbitals have non-zero values, and therefore finite non-zero densities, at the nucleus, the contributions to the Fermi contact term arise only from the orbitals with s-character.

The Hamiltonian for the contact term, as derived by FERMI [2, 3], is

$$\begin{aligned} H_c &= -\,(8\pi/3)\, g_e g_n \mu_B \mu_N \sum_i (\boldsymbol{I}\cdot\boldsymbol{s}_i)\, \delta(\boldsymbol{r}_i) \\ &= -\,(8\pi/3)\, (\mu_e/s)\, (\mu_I/I) \sum_i (\boldsymbol{I}\cdot\boldsymbol{s}_i)\, \delta(\boldsymbol{r}_i)\,, \end{aligned}$$

where $\delta(\boldsymbol{r}_i)$ is a three-dimensional delta-function, and the summation extends over all the s-electrons (for the reasons mentioned above). For an s-electron with α spin the value of the corresponding term in the summation is positive, while it is negative for an s-electron with β spin, and therefore the closed shells give no contribution to the Fermi contact. Therefore, only unpaired electrons need be considered and consequently one can write

$$H_c = -\,(8\pi/3)\, (\mu_e/s)\, (\mu_I/I)\, (\boldsymbol{I}\cdot\boldsymbol{s}) \sum \varepsilon_i\, \delta(\boldsymbol{r}_i)\,,$$

where ε_i takes the value ± 1 depending on whether the spin of the unpaired electrons considered is α or β. Taking into account that for an s-electron $l = 0$,

* This work has been supported in part by the National Research Council of Canada.

$j = s = \frac{1}{2}$ one obtains

$$2(\boldsymbol{I}\cdot\boldsymbol{s}) = 2(\boldsymbol{I}\cdot\boldsymbol{j}) = f(f+1) - I(I+1) - s(s+1)\,,$$

where the total angular momentum quantum number f assumes only the values $I \pm \frac{1}{2}$, and therefore

$$2(\boldsymbol{I}\cdot\boldsymbol{s}) = \begin{cases} I, & \text{for } f = I + \frac{1}{2}\,, \\ -(I+1), & \text{for } f = I - \frac{1}{2}\,. \end{cases}$$

Thus the energy splitting is then given by

$$\Delta E = (8\pi/3)\,\mu_e\,\mu_I(2 + 1/I)\,\varrho(0)$$

where $\varrho(0)$ is the electronic density at the nucleus corresponding to the s-orbital occupied by the unpaired electron. The corresponding hyperfine structure constant a_c is defined as

$$\begin{aligned} a_c &= 2\Delta E/(2I+1) = (16\pi/3)\,\mu_e\,\mu_I(1/I)\,\varrho(0) \\ &= 0.80021\cdot 10^3\,\mu_I(1/I)\,\varrho(0)\,, \end{aligned}$$

with μ_I expressed in the last term of this equation in units of nuclear magnetons.

The Table collects the value of a_c for the groundstates (^2S) of some neutral atoms, positive ions, and negative ions, evaluated from Hartree-Fock functions. The agreement between the present results and those of SACHS [*10*], evaluated from accurate analytical Hartree-Fock functions, is excellent; e.g., while SACHS [*10*] reports for Li^7 a value 289.55 Mc/sec for a_c, the value obtained in the present calculation is 290.871 Mc/sec. But unfortunately the experimental value, determined by KUSCH and TAUB [*6*], is 401.756 Mc/sec, and therefore it seems that Hartree-Fock functions are not appropriate for the evaluation of the hyperfine structure constants a_c.

Table. *Hyperfine structure constants a_c for the groundstates of various neutral atoms, positive ions, and negative ions*[a,b] (in Mc/sec)

System	M	a_c	System	M	a_c
Li	6	110	K	42	380
	7	291[c]	Cu	63	3561
Na	22	246		64	959
	23	625[d]		65	3813
	24	178	Be^+	9	512
K	38	259	Mg^+	25	465
	39	145[e]	Zn^+	67	1689
	40	180	Ca^+	43	580
	41	80	Ni^-	61	82

[a] Evaluated using the Hartree-Fock functions of CLEMENTI [*1*] and MALLI [*7*]. The values used for I and μ_I in these calculations are those quoted by RAMSEY [*9*].

[b] Existing experimental values, determined by KUSCH and TAUB [*6*], are: Li ($M = 7$), 401.756 Mc/sec; Na ($M = 23$), 885.805 Mc/sec; K ($M = 39$), 230.862 Mc/sec.

[c] SACHS [*10*] has calculated the values 289.55, 390.50, and 354.795 Mc/sec, using different functions (see the text), while NESBET [*8*] found a value of 396.7465 Mc/sec.

[d] SACHS [*10*] has obtained a value of 636.34 Mc/sec, and GOODINGS [*5*] reports the values 669 and 764 Mc/sec.

[e] GOODINGS [*5*] has reported the values 143 and 178 Mc/sec.

On the other hand SACHS [*10*], using projected unrestricted and unrestricted Hartree-Fock (PUHF and UHF, respectively) functions, obtains the values 354.795 and 390.50 Mc/sec, which represent a noteworthy improvement over the Hartree-Fock functions. NESBET [*8*], using a configuration interaction (CI) function, obtains a value within 1% of the experimental value.

Furthermore it can be seen from the Table that the agreement between the values of a_c, calculated from Hartree-Fock functions, and the experimental values becomes worse and worse for heavier atoms. However, an improvement for the a_c is achieved using PUHF, UHF, and CI functions, but unfortunately the improved values are still far away from the experimental values.

Mention can also be made of the values of a_c evaluated, using the SCF functions of FRAGA and BIRSS [*4*], for the $^{1,3}S$ states corresponding to the configuration $(1s)\,(2s)$ of He. These values are 9508 and 8348 Mc/sec, respectively.

References

[*1*] CLEMENTI, E.: Tables of atomic functions. International Business Machines Corporation, 1965.
[*2*] FERMI, E.: Z. Physik **60**, 320 (1930).
[*3*] — Mem. R. Acad. Ital. **4**, 131 (1933).
[*4*] FRAGA, S., and F. W. BIRSS: J. chem. Physics **40**, 3203 (1964).
[*5*] GOODINGS, D. A.: Physic. Rev. **123**, 1706 (1961).
[*6*] KUSCH, P., and H. TAUB: Physic. Rev. **75**, 1477 (1949).
[*7*] MALLI, G.: To be published.
[*8*] NESBET, R. K.: Physic. Rev. **118**, 681 (1960).
[*9*] RAMSEY, N. F.: Molecular beams. Oxford: Oxford University Press 1956.
[*10*] SACHS, L. M.: A theoretical study of simple many-electron systems, Report No. ANL — 6310, Argonne National Laboratory, May 1961.

Prof. SERAFIN FRAGA
Division of Theoretical Chemistry
Department of Chemistry
University of Alberta
Edmonton/Alberta Canada