Calculation of atomic hyperfine-field coupling constants

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The hyperfine fields characteristic of the free-atom valence s electron are calculated to form a consistent set of values for normalization of hyperfine fields obtained by NMR, Mössbauer, and other techniques in solids.

Hyperfine effects have provided one measure of electronic behavior in alloys and compounds. When comparing how alloying affects the hyperfine field $H_{\rm hf}$ of one atom with that of another it is desirable, as emphasized by Knight,¹ to normalize $H_{\rm hf}$ by the hyperfine field H_a , characteristic of the free-atom's valence *s* electrons. In this way, effects characteristic of the element in question are crudely separated from those associated with alloying.

A number of methods have been used by various authors¹⁻⁵ to obtain H_a , the hyperfine fields, due to outer s electrons, in free atoms. All of these authors are in agreement that the best method to obtain H_a for monovalent (alkali and noble) metals, is to use the measured atomic hyperfine-structure constants, usually from an atomic-beam experiment, combined with the nuclear moment and some fundamental constants. There is some (relatively small) numerical disagreement even for these elements. For the polyvalent atoms there is no straightforward experimental method of determining H_a and different calculational methods have been used. Knight¹ relied on atomic-beam measurements on excited ionic states and then corrected for the degree of ionization. Most of the other authors used the Fermi-Segrè-Goudsmit formula, with appropriate modifications and relativistic corrections. The results showed wide variations for some of the elements.

Previously, we introduced⁴ a scheme which we believe is superior, if only in internal consistency, to the other schemes currently employed. The purpose of the present comment is to extend and update our estimates. We are motivated by recent activity concerning hyperfine fields of impurity atoms in ferromagnetic iron. There is controversy between Campbell and Vincze⁶ on the one hand and Stearns⁷ on the other as to the origin of $H_{\rm hf}/H_a$ for these impurities: in the course of the arguments the two groups used different sets of H_a values. We too have inspected⁸ these hyperfine effects and have chosen to use our H_a values. There is more than a factor of 3 disparity among the estimates of H_a for some of the polyvalent pelectron metals. This does not severely affect the arguments made only because the $H_{\rm hf}$ for these impurities are almost zero. On the other hand, it is just these impurities which provide the best testing ground for Friedel screening ideas⁹ and for these it would be nice to resolve the choice of H_a .

Normalizing $H_{\rm hf}$ to the contact density appropriate to a valence *s* electron in the free atom is obviously an oversimplification, for there are other hyperfine effects, for example, core polarization from unpaired *p*, *d*, or *f* electrons. The purpose of the present exercise is, however, to estimate H_a and not to study these complications.

In our scheme, we employ Lindgren's relativistic Hartree-Fock program¹⁰ to calculate the magnetic contact density at the nucleus, $\rho(0)$, of a valence s electron for the neutral atomic configuration of interest. While H_a does not vary smoothly, the ratio of the experimental H_a to the calculated $\rho(0)$ does vary *almost* smoothly for the alkali and noble metals. Values of $H_a/\rho(0)$ are interpolated and multiplied by calculated $\rho(0)$'s to estimate H_a for the other elements. Groundstate atomic configurations are assumed except in the case of the transition metals where $d^n s^1$ configurations, most appropriate to the metals, are taken. The results are summarized in the Fig. 1 and Table I. Built into the interpolation scheme are, for example, any core-polarization effects associated with the *s* electron, assuming they scale smoothly as a function of atomic number Z with the direct interaction of the electron with the nucleus. The fact that the experimentally based $H_a/\rho(0)$ are not perfectly smooth in their variation causes some difficulties in the vicinity of Cs (Z=55) and Th (Z=90). The vertical bars on the figure indicate the uncertainties we attribute to this problem.

On the whole the H_a vary smoothly though there is a break in the curve on going from K to Ca and

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FIG. 1. Hyperfine field from the valence s electron in the free atom for the ground-state configurations, except for the transition elements, where $d^n s^1$ is taken. The crosses mark the H_a which have been experimentally determined. The lines have been drawn only to guide the eye between calculated points. The vertical lengths of the calculated data points represent errors due to ambiguities in interpolation (see text).

on to the 3*d* transition metals. (Sr was not calculated; we expect a break there as well.) The H_a rise sharply when the polyvalent atoms with open *p* shells are traversed: in such cases the *s* shell is contracting rapidly in towards the ion core.

TABLE I. Free-atom valence s electron hyperfine fields, H_a (MG). Values in brackets are experimentally determined. Atoms have been taken in their free-atom ground states except for the transition metals which have been assigned $d^n s^1$. Uncertainties, when given, are associated with the interpolation scheme (see text).

Z		H_a	Z		H _a	Z		H _a
3	Li	[0.122]	30	Zn	3.9	52	Те	21 ± 1
5	в	1.04	31	Ga	6.2	53	I	23 ± 1.5
6	С	2.1	33	\mathbf{As}	10.9	55	Cs	[2.04]
9	\mathbf{F}	8.6	34	Se	14	56	Ва	3.6 ± 0.2
11	Na	[0.394]	37	\mathbf{Rb}	[1.22]	72	$\mathbf{H}\mathbf{f}$	10.2 ± 0.5
13	Al	1.8	39	Υ	[2.35]	74	W	12.4 ± 0.4
15	\mathbf{P}	4.4	40	\mathbf{Zr}	2.65	75	Re	14.8 ± 0.4
19	К	[0.581]	41	Nb	3.05	77	\mathbf{Ir}	17.6 ± 0.2
20	Ca	1.1	42	Mo	3.5	78	\mathbf{Pt}	18.5 ± 0.1
22	Те	1.2	: 44	Ru	4.1	79	Au	[20.6]
23	V	1.4	45	$\mathbf{R}\mathbf{h}$	4.5	80	Hg	25
24	\mathbf{Cr}	1.55	46	Pd	4.8 ± 0.1	81	Tl	30
25	Mn	1.8	47	Ag	[4.95]	82	\mathbf{Pb}	36
26	Fe	1.95	48	Cd	7.2 ± 0.2	83	Bi	42
27	Co	2.2	49	In	10 ± 0.3	87	\mathbf{Fr}	3.7 ± 0.2
28	Ni	2.4	50	\mathbf{Sn}	13 ± 0.6	90	Th	6 ± 1
29	Cu	[2.60]	51	\mathbf{Sb}	16 ± 0.8			

The greatest disparity among the various predictions tends to occur here. For Al, for example, we, Campbell⁶ and Stearns⁷ obtain H_a values of 1.8, 0.87, and 0.5 MG, respectively. The situation is less severe for heavier elements: values of 36, 40, and 33 MG are obtained by the three groups, respectively, for Pb. Disagreements as large as 50% occur for the transition metals though (10-20)% is more typical.

The values of H_a for any but the monovalent metals result from a consistent interpolation scheme. While better calculations may be made in the future, these and any other alternative results cannot be directly tested by experiment.

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