Title
COMMENT ON. EMPIRICAL CORRECTION TO HARTREE-FOCK-SLATTER S-ELECTRON DENSITIES FOR CALCULATION OF CONTACT HYPER-FINE SPLITTINGS

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Comment on

EMPIRICAL CORRECTION TO HARTREE-FOCK SLATER S-ELECTRON DENSITIES FOR CALCULATION OF CONTACT HYPERFINE SPLITTINGS

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Mackey and Wood\textsuperscript{1} recently proposed an empirical correction to contact hyperfine structure constants. In their discussion they pointed out that the application of a relativity correction to electron densities calculated non-relativistically, or the use of relativistic wave functions will give hfs constants that are high by a factor 2. However they apparently used the relativity factor for the charge density, which depends on $f_0^2 + g_0^2$, rather than the factor for current density, which depends\textsuperscript{2} on $f_0 g_0$. Here $f_0$ and $g_0$ are the large and small components of the Dirac electronic wave functions, evaluated at the nucleus.

To calculate the magnetic hyperfine structure constant $a_s$ for a single impaired $s$ electron from $|\Psi(0)|^2$, the "nonrelativistic" electron density at the nucleus, the relativity factor

$$F_r(j,Z) = \frac{\hbar j(j+\frac{1}{2})(j+1)}{\rho(4\hbar^2 - 1)}$$

must be applied. Here

$$\rho = [(j+\frac{1}{2})^2 - a^2 z^2]^{1/2}$$

and $j = \frac{1}{2}$. 

1. Mackey and Wood
The factor $F_r(j, Z)$ accounts for the electron current density, which is relevant to magnetic interaction in the Dirac theory. Mackey and Wood have apparently used the relativistic charge density correction factor,\(^3\)

$$S(Z) = \frac{30(1+p)Y_0^{2p-2}}{(2p+1)(2p+3) \Gamma^2 (2p+1)}$$

where $Y_0 = 2ZR/a_0$ and $R$ is the nuclear radius. This factor is appropriate for isotope or isomer shifts, which are Coulombic in origin in the Dirac theory. It is much larger than $F_r(j, Z)$.

In Table I four factors are listed for the cases considered by Mackey and Wood: their ratio $a_{\text{exptl}}/a_{\text{nonrel}}$, $F_r(j, Z)$,\(^4\) their empirical factor, and the ratio $a_{\text{rel}}/a_{\text{nonrel}}$ given by them (this ratio is taken to be their relativity factor, because the exact value of $S(Z)$ depends on certain assumptions). The similarity for large $Z$ of the first three of these quantities suggests that the relativity factor $F_r(j, Z)$ accounts for much of the discrepancy between $a_{\text{exptl}}$ and $a_{\text{nonrel}}$. Thus their statement that consideration of the relativity factor will produce values of $a$ that are "high by a factor of 2 for large $Z" does not apply.

References

4. Ref. 1, Table 8.
Table I. Comparison of Relativity Factors

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<th>Z</th>
<th>$\frac{a_{exptl}}{a_{nonrel}}$</th>
<th>$F_r(J,Z)$</th>
<th>$\gamma$</th>
<th>$\frac{a_{rel}}{a_{nonrel}}$</th>
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