VI. ATOMIC BEAMS

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A. THEORY OF ATOMIC HYPERFINE STRUCTURE

A program of calculation of some atomic wavefunctions has been undertaken – using M.I.T.'s Whirlwind computer – in order to arrive at an accurate evaluation of the electronic matrix elements occurring in the theoretical formulas for atomic hyperfine structure (hfs).

1. Description of the Problem

Experimental observations, by optical or radio-frequency measurements, of the hyperfine structure of some atomic state are summarized by giving the values of the interaction constants, a, b, c, that represent the contribution of each multipole order to the level splittings. According to the theory each one of these interaction constants equals the product of a particular nuclear moment and an electronic matrix element. Thus, in order to find the nuclear moment accurately we must be able to evaluate the electronic matrix element accurately.

In the usual description of an atom most of the electrons are in closed shells of the core, and only one, or a few, electrons in the unfilled valence shell give rise to such angular properties as the hyperfine structure. This description is not rigorously correct, since the core is slightly distorted by the unsymmetrical motion of the valence electrons, and thus all the electrons do contribute something to the hyperfine structure. This many-particle aspect of the problem has been studied extensively by Sternheimer (1), but the exact magnitude of these corrections is not yet certain. The problem we are concerned with is that of calculating accurately the contribution of the valence electron(s) alone.

The best evaluation of these one-electron matrix elements previously given is that of Casimir (2). His approximation proceeds as follows. Since the integrals to be evaluated are of the form $\langle r^{-3} \rangle$, the most important contribution will come from the region of small r. Thus one needs to know the electronic wavefunction only in the region very close to the nucleus. Then by using the relativistic (Dirac) wavefunctions for an electron in a pure coulomb field at zero binding energy the various hfs integrals are evaluated analytically.

The first correction to this approximation would come from the effect of the shielding by all the other electrons on the wavefunction of the valence electron. If the total electrostatic potential of the atom is expanded in a power series about r = 0, the first term is of course $+Ze/r$ where Ze is the nuclear charge. The second term is the constant shielding potential of all the electrons, which may be estimated from the Thomas-Fermi

model as $-1.8Z^{4/3}\ e/a_o$, where a_o is the Bohr radius. These two terms of the total potential lead to an electronic wavefunction which in the region of small r may be described as a coulomb eigenfunction corresponding to a principal quantum number of $n \cong Z^{1/3}/1.9 \lesssim 2$; the Casimir approximation corresponds to $n = \infty$. This discrepancy in the wavefunctions is the reason for our present work.

Our program is to carry out the numerical integration of the one-electron Dirac wave equation with a potential that represents the entire atomic field, and then to calculate the integrals of interest in the study of hyperfine structure. The big problem is the choice of the potential. We have used a potential fashioned after a simple functional form discovered by Tietz (3) as an accurate approximation to the Thomas-Fermi function. We take

$$V = \frac{e}{r}\left[1 + (Z-1)/(1 + \beta r)^2\right]$$

as the potential seen by one electron in a neutral atom. The constant β is treated as a parameter which is so chosen that it will yield the best fit to the experimentally measured term values and fine structure for each atomic state calculated.

2. Calculations

The equations to be solved are

$$\left(\frac{d}{dr} - \frac{\kappa}{r}\right) f = \left(\frac{2}{\alpha} - \frac{\alpha}{2}\epsilon + \frac{\alpha}{e}V\right) g$$

$$\left(\frac{d}{dr} + \frac{\kappa}{r}\right) g = \left(\frac{\alpha}{2}\epsilon - \frac{\alpha}{e}V\right) f$$

where f and g are the radial eigenfunctions for the large and small components of the Dirac state vector, r is the distance from the nucleus measured in units of a_o, $\alpha = 1/137$, κ is an angular momentum quantum number, and ϵ is the energy eigenvalue measured in Rydbergs = $e^2/2a_o$. The integration of these equations is carried out by Whirlwind I by means of well-known numerical techniques.

First, with some given value of β (the potential parameter) the differential equations are integrated several times until the eigenvalue ϵ is found by a trial-and-error procedure. Then the normalization integral

$$\int_0^\infty (f^2 + g^2)\, dr$$

and the integrals of interest for hfs problems

$$\int_0^\infty (f^2 + g^2)\, r^{-3}\, dr, \quad \int_0^\infty f\, g\, r^{-2}\, dr, \quad \int_0^\infty f\, g\, r^{-4}\, dr$$

are calculated using the eigenfunctions. Also, the difference of the eigenvalues ϵ for two states of a doublet is just the fine-structure splitting δ. The entire calculation is repeated for another value of β, and the final results for all the quantities of interest are taken by interpolation at that value of β which best reproduces the experimental values of ϵ, δ, and $\int_0^\infty f\, g\, r^{-2}\, dr$ (which is fairly well-known from the hyperfine-structure a and the nuclear dipole moment). This routine requires about 1.5 hours of machine computation time for each doublet state.

3. Results and Future Plans

These calculations have been completed for the normal terms of Ga, In, Tl; and work is now in progress to do the same for Al, Cl, Br, I, and the second excited p-state of Cs. From the results thus far we find that ratios between the dipole and quadripole integrals and the fine-structure δ are only slightly different from the values given by Casimir's work. This happens because all of these depend mainly on the same quantity, $\langle r^{-3} \rangle$; and most of the large error in the wavefunction cancels out in ratios. However, the octopole integrals depend on $\langle r^{-5} \rangle$, and we find that these are considerably smaller than the values given by Casimir's approximation. As a result, the nuclear magnetic octopole moments in Ga and In are now found to be 20-25 per cent larger than those given in the previous evaluation (4).

It is also believed that some of the results of these calculations will help shed light on the many-electron (core polarization) problem. A thorough report and an evaluation of the completed calculations will be prepared for later publication.

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References

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