Progress Report

for

Theoretical Hyperfine Structure Constants for Transition Metal Atoms and Ions

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Accurate calculation of hyperfine structure of $(d+s)^n$ states presents a considerable computational challenge because it necessitates simultaneously dealing with relativistic and correlation effects in a multi-reference framework (i.e. all $(d+s)^n$ states of fixed n, J treated at once).

We spent about half of the period improving the algorithms, as follows: (1) Introduction of the relativistic BCB method[1] to allow angular momentum eigenstates (J^2, J_z) to be created for basis sets of several thousand determinants, (2) further automating the relativistic REDUCE method[1] which constructs the smallest possible N electron basis set for each configuration, so as to provide an energy matrix of "manageable" order (≤ 2000), (3) Speeding up [2] a large order multi-root diagonalizer recently added to our codes, and (4) coding up the nuclear quadrupole operator, to allow prediction of nuclear quadrupole moments, when experimental measurement is available.

This methodology was then applied in a thorough study of the hfs of Zr II for $(d+s)^3$ states. We found (see Table I) the fs intervals were determined to within 0.075 eV (the uppermost 2D missing from Moore[3] was confirmed to be where Kiess[4] suggested it would be), and the hfs was found to be only 17% in error as compared to the very recent measurements of 5 of the levels, made by Linda Young et al[5] of ANL. A new prediction for the nuclear quadrupole moment, Q , was also made. This accuracy should be contrasted to Dirac-Fock results, which frequently yield the incorrect sign for hfs constants of $(d+s)^3$ levels[5]. For the first time, all of the $(d+s)^n$ fs levels have been accurately determined by *ab initio* theory. This indicates that we have identified all the important correlation effects for fs; this should benefit theorists working on molecules and solids having transition metal

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atoms.

A time consuming part of our calculations is assembling a sound, thorough set of data — in particular, just what should constitute the one and N electron basis sets? With these established for Zr II, it was thought that these may be applicable to species iso-electronic and iso-group to Zr II, providing the ordering of states within the $(d+s)^3$ manifold did not vary substantially. Calculations have now been done for Nb III, La I and Hf II [J=1.5] which confirm this idea; these calculations, which include predictions for positions of levels so far un-observed will be published once the J=0.5 calculations are complete.

In addition to references [1],[2] and [5], two articles on Ti II hfs have been written up [6,7], and two talks will be given [8,9] at the DAMOP meeting in Reno, Nevada in May of 1993. A new student, supported by DOE, Konstantin Dinov has joined the project.

References:

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- [3] C. E. Moore, Atomic Energy Levels, Vol. II NSRDS-NBS35, US GPO, Washington, D. C. 1971.
- [4] C. C. Kiess, J. Opt. Soc. Am. **43**, 1024 (1953).
- [5] L. Young, C. A. Kurtz, D. R. Beck and D. Datta, "Hyperfine Studies in Zr II: Experiment and Relativistic Configuration Interaction Results", Phys. Rev. A, to appear.
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- [7] N. Berrah, C. Kurtz, L. Young, D. R. Beck and D. Datta, "High Precision Laser Measurements of the Hyperfine Structure in $^{49}\text{Ti II}$ ", Nuc. Inst. Meth., to appear.

[8] D. Datta and D. R. Beck, "Hyperfine Structure of Zr II and Nb II (d+s)ⁿ States", Bull. Am. Phys. Soc., to appear.

[9] K. Dinov and D. R. Beck, "Improvement of Convergence for Weber's Large Order Multi-Root Diagonalizer", Bull. Am. Phys. Soc., to appear.

Table I: Fine and Hyperfine Structure of ZrII J=3/2 (d+s)³ States. The labeling of the levels (first two columns) is that given by Moore[3] as corrected by Kiess[4]. The experimental energy is also drawn from these two sources. All other quantities are from ref. [5]; the results marked CI are obtained by the relativistic many-body calculation; those marked DF are Dirac-Fock results as obtained from CI calculations.

Level		Energy (cm ⁻¹)		A (MHz)		B(MHz)/Q(b)	B(MHz)
Config.	SLJ	Experiment	Theory	Theory	Expt.	Theory	Expt.
4d ³	² D	27699.96	29066				
4d ³	² P	20080.30	20710	111.5(CI) -76.0(DF)	109.7678	-138.4(CI) -33.9(DF)	33.716
4d 5s ²	² D	14298.64	14996				
4d ³	² D	13428.50	14387				
4d ³	⁴ P	9742.80	10072	134.1(CI) -56.4(DF)	110.1774	-133.3(CI) -156.2(DF)	34.713
4d ² 5s	⁴ P	7736.02	8209				
4d ² 5s	² P	6111.70	6788				
4d ² 5s	² D	4248.30	5084	190.3(CI) 375.1(DF)	199.2498	-28.8(CI) -83.8(DF)	7.706
4d ³	⁴ F	2572.21	2950				
4d ² 5s	⁴ F	0.00	0.00				

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