PHYSICAL REVIEW A VOLUME 52, NUMBER 5 NOVEMBER 1995

Relativistic many-body effects in the fine and hyperfine structure of ^{139}La II $(5d+6s)^2$ $J=2$ states: The need for second-order electrostatic corrections

Debasis Datta* and Donald R. Beck
Physics Department, Michigan Technological University, Houghton, Michigan, 49931

(Received 24 July 1995)

Using our relativistic-configuration-interaction methodology, we report multireference calculations of energy differences and magnetic-dipole and electric-quadrupole hyperfine structure constants of all five levels in the $(5d+6s)^2$ $J=2$ manifold of singly ionized ^{139}La. The errors in the splittings of the bottom four levels are no more than 0.02 eV, while the separation of the two highest levels has an error of 0.11 eV due to an incomplete description of the correlation in the levels belonging to higher manifolds. The hyperfine-structure constants show strong sensitivity to many-body effects, resulting in striking improvements over the multiconfiguration Dirac-Fock values. Seven of the ten hyperfine constants are accurate within 2–12 %. For the rest of the constants we have identified the primary cause of the errors as an incorrect description of many-body effects in the high-lying levels and have discussed possible remedies.

PACS number(s): 31.30.Gs, 31.25.Jf, 31.30.Jv

I. INTRODUCTION

This work is a continuation of our efforts towards developing a cohesive and rigorous relativistic-configuration-interaction methodology that will address the bound-state properties of the entire Periodic Table in a systematic fashion. In our previous work on three- [1] and four- [2,3] electron systems such as Zr II and Nb II, we have shown that it is not only possible to position the low-lying $[nd+(n+1)s]^N$ levels of the transition metals with reasonable accuracy (a few hundred cm^{-1}), but it is also possible to use the variational wave function to carry out an accurate perturbative calculation of the hyperfine structure (hfs) of these levels. Since the magnetic-dipole (A) and electric-quadrupole (B) constants have been measured for the entire $(5d+6s)^2$ manifold for La II [4], and based on our work on the hyperfine structure of Sc II and Y II [5], we expect large many-body effects to exist; it presents an extremely interesting system for a first-principles theoretical study. To our knowledge such a study does not exist, although calculations of the La II hfs using the classical parametric scheme have been carried out by Bauche *et al.* [6].

Relativistically, one is confined to work within a given J of the atomic states. Accordingly, we pick the $J=2$ "multiplet" since it contains the single largest number of levels, namely, five of them. These correspond to each of the $5d_{3/2}^2$, $5d_{3/2}5d_{5/2}$, $5d_{5/2}^2$, $5d_{3/2}6s$, and $5d_{5/2}6s$ configurations, which serve as the reference (or the zeroth-order) functions of our calculation. Computationally speaking, the problem is considerably simpler compared with, say, either Nb II $J=2$ $(4d+5s)^4$ states (21 references) or Zr II $J=3/2$ states (10 references). The system poses quite a challenge to the theory, however; a multiconfiguration Dirac-Fock (MCDF) calculation on the five $(5d+6s)^2$ vectors yields a poor hfs, with two of the A's even having incorrect signs. Due to the strongly interacting nature of the nd^N and $nd^{N-1}(n+1)s$ states, it is absolutely essential that the relative energies of the $5d^2$ and $5d6s$ levels are accurately determined before the hfs is calculated.

To this aim, we first carry out a thorough multireference relativistic configuration interaction calculation of the La II $J=2$ $(5d+6s)^2$ manifold. The core-polarization effects important for hfs are included once a satisfactory theoretical level spectrum is obtained. The hfs constants are determined from the diagonal (in J) contributions to the hyperfine splitting. A concise description of the theoretical formalism including a brief contemporary review of the hfs calculations can be found in Ref. [2].

II. CALCULATIONS

The atomic wave function is a superposition of the zeroth-order vectors and a chosen class of angular momentum (J^2 and J_z) eigenstates. These are formed from the MCDF vectors by one- and two-electron excitations. To first order, these are the only nonvanishing contributors to the energy. Such excitations could be into the holes in the Dirac-Fock (DF) space or into the external unoccupied orbitals. The latter are represented as virtual spinors (vlj or vl_j or simply vl). We categorize the J^2 eigenkets, known more popularly as the configuration-state functions according to the following scheme.

(i) The MCDF vectors, or all the vectors in the $(5d+6s)^2$ manifold, consist of the zeroth-order vectors and excitations of the types $n_1l_1j_1 \rightarrow n_2l_2j_2$ and $(n_1l_1j_1)^2 \rightarrow (n_2l_2j_2)^2$, where the nlj sets refer only to the $5d$ or the $6s$ orbital.

(ii) The valence-shell correlation configurations arise from single excitations $nl_1j_1 \rightarrow vl_2j_2$ or the pair excitations such as $n_1l_1j_1, n_2l_2j_2 \rightarrow vl_3j_3, v'l_4j_4$. Again, the nlj sets represent only the valence spinors.

(iii) The core-valence correlation configurations are the double excitations involving a valence and a core electron and also fall into the general category of $n_1l_1j_1, n_2l_2j_2 \rightarrow vl_3j_3, v'l_4j_4$. However, only one of the two nlj sets belong to either $5d$ or the $6s$ orbital.

---

*Present address: Department of Electrical Engineering, Michigan Technological University, Houghton, MI 49931.

(iv) The core-core correlation configurations can be either of the type $n_1l_1j_1,n_2l_2j_2 \rightarrow n_3l_3j_3,n_4l_4j_4$; $n_1l_1j_1,n_2l_2j_2 \rightarrow n_3l_3j_3,vl_4j_4$; or $n_1l_1j_1,n_2l_2j_2 \rightarrow vl_3j_3,v'l_4j_4$. Subscripts 1 and 2 belong to the core electrons and 3 and 4 to the valence spinors.

(v) Finally, the core polarizations, or the single excitations from the core, look either like $n_1l_1j_1 \rightarrow n_2l_2j_2$ or like $nl_1j_1 \rightarrow vl_2j_2$. A large number of such excitations, especially the ones from the deeper core, are not significant energetically but can be critical contributors to the hyperfine structure.

The DF spinors are the numerical solutions of the MCDF equations obtained on a logarithmic mesh [7] and the virtual spinors are taken to be the relativistic screened hydrogenic functions (RSHFs) [8]. The RSHFs are parametrized through their characteristic nuclear charge Z^*, which is optimized during the variational process. This way, only a handful of virtual spinors of a particular symmetry can effectively describe the entire Rydberg series of the same symmetry. Use of RSHFs also circumvents the well known [9] problem of "variational collapse," the uncontrolled dissolution of the energy into the negative continuum during the variation of an analytic spinor.

The atomic Hamiltonian is the Dirac-Coulomb Hamiltonian. Although the Breit term in the next most important correction to the Hamiltonian, its effect on the relative positions of the nd^N and $nd^{N-1}s$ levels is usually quite small compared with the correlation corrections. In the present case, we actually find that the differential contributions from the Breit term does not exceed 80 cm^{-1} ($\approx$0.01 eV) at the MCDF level. This is also considerably smaller than the accuracy that we have achieved so far for the second-row transition-metal ion energy levels [1–3].

In a multireference framework, the DF spinors derived from a particular root must be used for all levels and the choice of the root depends on one's concern and intuition at the initial phase of formulating the problem. A preliminary MCDF calculation shows that the magnetic-dipole hyperfine constants (the A's) are quite poor for the $5d^2\,{}^3P$ and the $5d6s\,{}^3D$ levels, both having the wrong sign. In order to best describe these two states, we obtain the $(1s,\ldots,5d)$ radials from a MCDF calculation [10] on the $5d^2\,{}^3P$ root and extract the $6s$ radial from a separate calculation on the $5d6s\,{}^3D$ root. The $6s$ radial thus obtained is reorthogonalized to the $1s,\ldots,5s$ radials. The angular parts of the spinors are the same as those of the corresponding hydrogenic functions. Corrections to the radial characteristics for the other roots are incorporated through the symmetry preserving single excitations $5d_j \rightarrow vd_j$ and $6s \rightarrow vs$ at the valence configuration-interaction (CI) stage. If the variational steps are carefully carried out, the choice of the roots from which the DF spinors are derived does not affect the end results [11] however.

The inclusion of many-body effects begins by first identifying the valence correlations and choosing the virtual space so that at least 95% of the valence correlation energy is accounted for. To minimize the errors due to possible radial inadequacies, we also include the nearest even-parity configurations, namely, those belonging to the $4f6p$ configurational manifold, the lowest of which is at 35 452.66 cm^{-1} [12]. It must be noted that the topmost $(5d+6s)^2$ level is $5d^{2\,1}D$ at 10 094.86 cm^{-1} [12]. We optimize two sets of virtual spinors spanning vs through vg and considering all significant single and pair excitations $[5d,6s \rightarrow vs,vd,vg;(5d+6s)^2 \rightarrow (4f+6p)vl,vlvl'$ subject to $|l-l'| \leq 2]$. Expanding the basis set to include a single vh essentially demonstrates that this provides a near-complete description of the valence correlation.

The strongest correlation contributions, both absolute and differential, come from the shallow core, i.e., from excitations involving the $5p$ spinors to be precise. Of these, the most dominant ones are $5p \rightarrow vp,vf;5p^2 \rightarrow (5d+6s)^2$, $(5d+6s)vd$; and $5p5d \rightarrow vpvd,vdvf,vfvg$. Between $5d^2$ and $5d6s$ manifolds, contributions from each of these differ by several tenths of an eV, bringing about the most dramatic corrections to the relative positions of the energy levels. One should note that the differential importance of the designated $5p^2$ excitations is due to exclusion effects associated with the Pauli principle. Also present are the other important but comparatively less dominant ones: $5p \rightarrow vh$; $5p^2 \rightarrow (5d+6s)vg,(5d+6s)vs$; and $5p5d \rightarrow vsvp,vsvf,vpvg,vgvh,vdvh$, whose effects are about an order of magnitude smaller. At this stage, we add one additional virtual spinor for each symmetry within the range $l \leq 3$.

Naturally, the next step in this problem would be to explore the many-body effects arising from the $5s$ shell. Pair correlations such as $5s5p \rightarrow 5dvp,5dvf$; $5s5d \rightarrow vsvd$; and $5s \rightarrow 5d,vd,vs$ were found only to have a modest effect, all others from $5s5d$ being negligible. The single excitations $5s \rightarrow 6s,vs$ also play crucial roles in determining the hyperfine structure of the energy levels, a fact that is well known. Other possible double excitations, e.g., those arising from $5s^2$, were seen to have little effect on the energy and were omitted. A detailed listing of the various contributors is given in Table I. As is obvious from the table, we have discussed here only those effects that reflect a difference of 0.01 eV or higher between the $5d^2$ and $5d6s$ configurational manifolds. Our final CI matrix consisted of over 6000 vectors.

So far, we have not illuminated the computational challenge associated with such a calculation. Many of the core-valence and core-core correlations generate several thousand eigenvectors per configurational manifold. Each of these eigenvectors may again contain thousands of determinants. The contribution of the angular-momentum eigenstates and the matrix elements of the Hamiltonian could thus become the bottlenecks in the calculation [2]. As discussed in our prior work [1,13], we have implemented the Bartlett-Condon-Beck (BCB) and the REDUCE computer algorithm to deal with these two situations respectively in a very efficient manner. The angular-momentum eigenstate are constructed by splitting each configuration into two parts and reassembling them using the BCB method. The large number of eigenvectors thus created are transformed into a minimal set by the REDUCE method and keeping only those members that survive in the nonrelativistic limit. The efficiency gain and accuracy of these procedures have been discussed in Ref. [1].

Since the level energies are quite well positioned with respect to each other at this point, it seems logical to shift the focus of the problem to the hfs constants. Seven of the ten hfs constants are found to be in excellent agreement with experiment, namely, the A's for the $5d^2\,{}^3F$, ${}^3P$, ${}^1D$, $5d6s\,{}^1D$, and ${}^3D$ levels and the B's for the $5d^2\,{}^3F$ and

TABLE I. First-order contributions (in eV) of single and pair correlations to the various $(5d+6s)^2$ $J=2$ states in La II. All signs are reversed. MCDF contributions are only from the vectors outside the reference manifold. The numbers in brackets denote multiplicative powers of 10.

Excitation	$5d6s\ {}^1D$	$5d^2\ {}^3P$	$5d6s\ {}^3D$	$5d^2\ {}^1D$	$5d^2\ {}^3F$
MCDF	−0.647[0]	0.278[−02]	0.583[−01]	0.508[0]	0.545[−01]
$(5d+6s)^2\rightarrow 4f6p$	0.581[−01]	−0.522[−04]	0.259[−01]	−0.432[−02]	0.233[−02]
$\rightarrow 6p^2$	0.921[−01]	0.112[−01]	0.430[−03]	−0.745[−02]	−0.471[−03]
$\rightarrow 4f^2$	0.273[−04]	0.424[−01]	−0.158[−04]	0.282[−01]	0.153[−01]
$6s\rightarrow vs$	0.264[−02]	0.975[−04]	0.529[−01]	0.379[−01]	0.484[−02]
$\rightarrow vd$	0.193[−01]	−0.146[−04]	0.391[−02]	0.320[−02]	0.965[−02]
$\rightarrow vg$	0.669[−01]	−0.850[−04]	0.516[−02]	0.113[−01]	0.148[−01]
$5d\rightarrow vd$	0.127[0]	−0.551[−04]	0.556[−01]	−0.465[−02]	−0.390[−03]
$(5d+6s)^2\rightarrow 6pvp$	0.567[−01]	0.106[−01]	0.197[−02]	−0.409[−02]	−0.859[−04]
$\rightarrow 6pvf$	0.112[0]	−0.116[−03]	0.387[−01]	−0.998[−02]	0.506[−02]
$\rightarrow 4fvp$	0.310[−01]	−0.361[−04]	0.107[−01]	−0.239[−02]	0.214[−02]
$\rightarrow 4fvf$	0.171[−01]	0.812[−01]	−0.619[−03]	0.433[−01]	0.286[−01]
$\rightarrow 4fvh$	0.238[−02]	−0.264[−05]	−0.729[−04]	0.194[−02]	0.103[−02]
$\rightarrow vp^2$	0.183[−01]	0.443[−02]	0.486[−03]	0.873[−04]	0.229[−03]
$\rightarrow vd^2$	0.598[−02]	0.383[−01]	0.124[−04]	0.350[−01]	0.255[−01]
$\rightarrow vf^2$	0.243[−01]	0.702[−01]	−0.854[−03]	0.347[−01]	0.253[−01]
$\rightarrow vg^2$	0.867[−02]	0.228[−01]	−0.309[−03]	0.110[−01]	0.621[−02]
$\rightarrow vsvd$	0.181[−01]	−0.111[−04]	0.155[−01]	−0.333[−03]	0.454[−04]
$\rightarrow vpvf$	0.589[−01]	−0.736[−04]	0.158[−01]	−0.536[−02]	0.450[−02]
$\rightarrow vdvg$	0.716[−02]	−0.122[−04]	0.425[−02]	0.343[−02]	0.165[−02]
$5p\rightarrow vp$	0.262[0]	0.813[−01]	0.365[0]	0.965[−01]	0.855[−01]
$\rightarrow vf$	0.483[0]	0.761[0]	0.468[0]	0.723[0]	0.777[0]
$\rightarrow vh$	0.152[−01]	0.220[−01]	0.147[−01]	0.235[−01]	0.295[−01]
$5s\rightarrow vs$	0.184[−01]	0.585[−02]	0.144[−01]	0.178[−02]	0.545[−02]
$\rightarrow vd$	0.405[−01]	0.504[−01]	0.247[−01]	0.236[−01]	0.304[−01]
$\rightarrow (5d+6s)$	0.159[−01]	0.462[−01]	0.237[−01]	0.324[−01]	0.177[−01]
$5p^2\rightarrow (5d+6s)^2$	0.704[0]	0.588[0]	0.693 [0]	0.566[0]	0.548[0]
$\rightarrow (5d+6s)vd$	0.871[0]	0.779[0]	0.871[0]	0.776[0]	0.772[0]
$\rightarrow 5dvg$	0.103[0]	0.949[−01]	0.103[0]	0.930[−01]	0.924[−01]
$\rightarrow 5dvs$	0.139[−01]	0.167[−01]	0.134[−01]	0.160[−01]	0.159[−01]
$\rightarrow vp^2$	0.871[−01]	0.942[−01]	0.886[−01]	0.950[−01]	0.951[−01]
$\rightarrow vd^2$	0.311[0]	0.316[0]	0.314[0]	0.317[0]	0.315[0]
$\rightarrow vf^2$	0.266[0]	0.262[0]	0.269[0]	0.267[0]	0.268[0]
$\rightarrow vpvf$	0.165[−01]	0.165[−01]	0.165[−01]	0.162[−01]	0.168[−01]
$5p5d\rightarrow vsvp$	0.461[−01]	0.147[−01]	0.503[−01]	0.158[−01]	0.145[−01]
$\rightarrow vpvd$	0.185[0]	0.224[0]	0.201[0]	0.224[0]	0.233[0]
$\rightarrow vdvf$	0.203[0]	0.325[0]	0.204[0]	0.329[0]	0.336[0]
$\rightarrow vfvg$	0.104[0]	0.181[0]	0.103[0]	0.183[0]	0.184[0]
$\rightarrow vgvh$	0.187[−01]	0.313[−01]	0.185[−01]	0.316[−01]	0.317[−01]
$\rightarrow vsvf$	0.123[−01]	0.256[−01]	0.127[−01]	0.282[−01]	0.293[−01]
$\rightarrow vpvg$	0.498[−02]	0.899[−02]	0.471[−02]	0.961[−02]	0.100[−01]
$\rightarrow vdvh$	0.435[−02]	0.826[−02]	0.437[−02]	0.867[−02]	0.872[−02]
$5s5d\rightarrow vsvd$	0.140[−01]	0.292[−01]	0.139[−01]	0.289[−01]	0.299[−01]
$\rightarrow vpvf$	0.376[−02]	0.763[−02]	0.357[−02]	0.789[−02]	0.685[−02]
$\rightarrow vs^2$	0.829[−03]	0.000[0]	0.773[−03]	0.000[0]	0.000[0]
$\rightarrow vp^2$	0.180[−02]	0.247[−02]	0.222[−02]	0.269[−02]	0.221[−02]
$\rightarrow vd^2$	0.894[−02]	0.826[−02]	0.909[−02]	0.777[−02]	0.855[−02]
$\rightarrow vf^2$	0.105[−01]	0.123[−01]	0.108[−01]	0.111[−01]	0.119[−01]
$5s5p\rightarrow 5dvp$	0.692[−01]	0.856[−01]	0.693[−01]	0.867[−01]	0.878[−01]
$\rightarrow 5dvf$	0.245[0]	0.221[0]	0.245[0]	0.219[0]	0.217[0]
$4p\rightarrow vp$	0.767[−03]	0.834[−03]	0.692[−03]	0.473[−03]	0.489[−03]
$\rightarrow vf$	0.285[−02]	0.691[−02]	0.284[−02]	0.406[−02]	0.333[−02]

TABLE I. (*Continued*).

Excitation	$5d6s\ ^1D$	$5d^2\ ^3P$	$5d6s\ ^3D$	$5d^2\ ^1D$	$5d^2\ ^3F$
$4s\rightarrow vs$	0.841[−04]	0.202[−04]	0.120[−03]	0.597[−05]	0.186[−04]
$\rightarrow vd$	0.105[−03]	0.312[−03]	0.754[−04]	0.233[−03]	0.256[−03]
$\rightarrow(5d+6s)$	0.387[−05]	0.215[−05]	0.194[−05]	0.425[−06]	0.219[−05]
$3p\rightarrow vp$	0.177[−04]	0.101[−04]	0.189[−04]	0.558[−05]	0.615[−05]
$3s\rightarrow vs$	0.770[−05]	0.108[−05]	0.818[−05]	0.798[−06]	0.904[−06]
$\rightarrow vd$	0.838[−06]	0.294[−04]	0.800[−05]	0.260[−04]	0.212[−04]
$\rightarrow(5d+6s)$	0.202[−06]	0.316[−06]	0.193[−06]	0.148[−06]	0.140[−06]
Total	0.422[+01]	0.461[+01]	0.452[+01]	0.493[+01]	0.448[+01]

^1D levels. The inclusion of core polarizations $4p\rightarrow vp,vf$ and $4s\rightarrow vs$ also brings the $5d^2\ ^3P$ electric-quadrupole constant to similar agreement, although they mostly provide only marginal improvements to the rest. The insertion of $3s\rightarrow vs$ and $3p\rightarrow vp$ along with further expansion of the virtual basis does not yield any significant changes or improvements. Therefore, we now turn to carry out a careful analysis of the problem.

III. RESULTS AND ANALYSES

The relative energies of the $(5d+6s)^2$ levels are quite well determined; in order of increasing energies, the splittings between the adjacent levels differ (in wave numbers) by 51.48, 14.81, 163.4, and 1106.63, respectively (Table II) from the corresponding experimental values [12]. The error in the topmost level is inherent in a restricted variational treatment such as a "first-order" CI, as discussed below. Four of the five magnetic-dipole constants are determined within 7 − 12 % and three of the electric-quadrupole constants are determined within 2.5–10.5 %. Theoretically derived *LS* identities of the roots agree well (Table II) with that of Martin, Zalubas, and Hagan [12].

We have identified very likely all major first-order many-body effects in this system (Table I), i.e., those contributing ~0.10 eV or more to the energy differences between the $5d^2$ and $5d6s$ manifolds and most of those in the 0.01–0.10 eV range. The unaccounted for correlation energies must come from the cumulative effects of differential contributors of the order of ~0.01 eV or even smaller. Many of these would cancel each other. Also, further refinements to the energy levels must also take into account the (i) Breit contributions and (ii) second-order corrections emerging from a more accurate description of the high-lying states. Our failure to take into consideration the many-body effects in those states is responsible for the comparatively large error in the topmost level ($5d^2\ ^1D$) of the manifold of our interest, viz., $(5d+6s)^2$.

From the standpoint of first-order perturbation theory, the position of a particular level is mainly determined by its interaction with the levels right above and below it. Preferential inclusion of many-body effects in the lowest manifold effectively causes it to move further down, thus forcing a much reduced interaction between the highest level in the manifold and the "external" levels higher up in the spectrum. This precisely is the cause of the seemingly large error in the $5d6s\ ^1D$ state. Since the total correlation contribution to each of the $(5d+6s)^2$ vectors add up to ~4.0 eV, their

TABLE II. *Ab initio* energies and hyperfine structure of La II $J=2$ $(5d+6s)^2$ states. The values within parentheses are the MCDF values. See the text for an explanation of the discrepancies between the experimental and the CI values in a few of the hyperfine constants. Only the highest *LS* components have been shown in the extreme right columns. The values of the nuclear parameters are $I=\frac{7}{2}$, $\mu=2.778$, and $Q=0.22$ b [14].

Level (Expt.^{a})		Energy (cm^{-1})		A (MHz)		[B (MHz)]/[Q (b)]		Level (Theor.^{b})	
Configuration	$^{(2S+1)}L$	Theor.^{b}	Expt.^{a}	Theor.^{b}	Expt.^{c}	Theor.^{b}	Expt.^{c}	Dominant configuration	Leading *LS* component (%)
				53.86	48.12	161.02	180.00	$5d6s$	52.2 ^1D
$5d6s$	^1D	11 071.46	10 094.86	(91.07)		(129.74)		$5d^2$	36.6 ^1D
				−141.43	−158.11	−209.55	−204.54	$5d^2$	63.8 ^3P
$5d^2$	^3P	6 427.39	6 227.42	(89.45)		(−191.81)		$5d^2$	25.2 ^3F
				−6.40	−8.69	156.42	257.72	$5d6s$	75.6 ^3D
$5d6s$	^3D	2 628.17	2 591.60	(183.73)		(127.16)		$5d^2$	16.1 ^1D
				842.85	948.83	136.96	226.36	$5d^2$	71.4 ^1D
$5d^2$	^1D	1 445.94	1 394.46	(529.25)		(55.07)		$5d6s$	16.2 ^3D
				368.75	397.32	84.56	90.00	$5d^2$	60.7 ^3F
$5d^2$	^3F	0 000.00	0 000.00	(253.53)		(77.41)		$5d^2$	27.9 ^3P

[a] Reference [12].

[b] This work.

[c] Reference [4].

separations from the high-lying levels suffer from a similar additive error. We will return to prescribing appropriate corrective measures soon.

The magnetic-dipole constants show strong sensitivity to many-body effects and result in remarkable improvements over the MCDF values (Table II). The two largest constants, namely, those for the $5d^2\ ^3F$ and $5d^2\ ^1D$ levels are determined to within less than 7.2% and 11.2%, respectively, while those for the $5d^2\ ^3P$ and $5d6s\ ^1D$ levels are correct to 10.5% and 11.9%, respectively. The $5d6s\ ^3D$ constant is tiny (experimental value -8.69 MHz [4] and despite being within ~ 2 MHz, the CI value has an error of 26.3%.

Further improvement of the dipole constants is complicated by the fact that the hyperfine constants of the $5d6s\ ^3D$ level are extremely sensitive to its splitting with the neighboring $5d^2\ ^1D$ state. This is evidenced by observing the changes in hfs and CI coefficients between two subsequent stages of the calculation. Using the normalized coefficients for the $5d6s$ vectors from the two last stages, we obtain DF hyperfine constants differing by as much as ~ 50 MHz while the MCDF coefficients vary only by $\sim 2-3$ %. The error of about 10.6% (~ 100 MHz) in the $5d^2\ ^1D$ level is likely to be associated with the incorrect position of the $5d6s ^1D$ level, both of which are heavily mixed.

The electric-quadrupole constants are comparatively less sensitive to the many-body effects. Nonetheless, all of them show very impressive improvements over the corresponding MCDF values, resulting in accuracies of 6.0% ($5d^2\ ^3F$), 2.4% ($5d^2\ ^3P$), and 10.5% ($5d6s\ ^1D$). Evidently, the relatively large departure (greater than 39%) in the B's for the first and second excited states arise from effects beyond the first-order many-body corrections to the wave function. A close scrutiny of the contributions to the electric-quadrupole constants reveals that the largest effects come from the interaction of some of the levels appearing high up in the spectrum. In the present case, the eigenvectors are those corresponding to the $6svd$ configurations, one of which, according to Martin, Zalubas, and Hagan [12], is located at 64 529.9 cm^{-1}, the other one being unidentified. These levels however, are by and large poorly described due to the absence of core-core and core-valence correlation effects associated with them, which are included in the $(5d+6s)^2$ manifold, as mentioned earlier in this section. Consequently, many-body corrections to their positions would result in an increased contribution to the hyperfine interaction energy, presumably correcting the quadrupole constants. Inclusion of such effects also corrects the position of the highest levels of the $(5d+6s)^2$ manifold. As far as we know, such a conjecture is being made and put forth in the literature for the first time.

A fairly large number of levels appear between the $(5d+6s)^2$ manifold and the continuum, only a few of which contribute to the hfs. For open d and f systems simultaneous many-body treatment of all these levels belonging to various manifolds is an impossibility at this stage. Until this can be accomplished, a semiempirical treatment based on experimental energies and theoretically known magnitudes of many-body effects could conceivably be devised. Clearly, such a treatment would be completely *ab initio* to first order; only the second-order effects, wherever necessary, would have to be incorporated in a semiempirical fashion.

We have begun introducing such corrections *ad hoc*, by adding to the diagonal matrix elements corresponding to the higher levels, an energy equal to the total accounted for core-core and core-valence correlation in the $(5d+6s)^2$ manifold, which is about -4.0 eV. We do see the expected trends: a significant ($\sim 45\%$) improvement in the position of the topmost $5d^2\ ^1D$ level and a 10–15 % improvement in the quadrupole constant B's of the $5d6s$ levels. The differential effects between these levels remain to be determined, for which the experimental level splittings may be taken as guidelines. The combination of a large number of levels and our use of virtual spinors instead of well defined $6d$ and $7s$ radial functions make further semiempirical calculation unfruitful. Before proceeding further along these lines we will have to introduce $6d$ and $7s$ spinors obtained from an MCDF calculation. Since this whole process is a nonlinear one, we are looking into developing a suitable fitting mechanism that will help determine these shift parameters more accurately and avoid any trial and error. Eventually, the parametrized second-order treatment will be replaced in phases, with a larger and more robust relativistic-configuration-interaction algorithm.

The most expensive stage of the calculation is constructing the angular structure. Once the structure for all the matrix elements are set up, they are temporarily stored on the hard drive to allow for the memory to be used for setting up the radial integrals and the matrix elements themselves. The structure files are normally very large (0.6−1.0 Gbyte) and the lack of available disk space had required us to generate them "on the fly" for every single calculation, thus increasing computational costs enormously. To alleviate this difficulty, we have recently acquired a 4.0-Gbyte disk drive that allows us to save the structure generated for use in a subsequent calculation that has an identical eigenvector set with similar radials. In the present case, this has resulted in a time savings by a factor of about 4.5.

IV. CONCLUSIONS

We have performed a perturbative first-order calculation of the magnetic-dipole and electric-quadrupole constants of the five $(5d+6s)^2$ levels of La II $J=2$ using a multireference relativistic-configuration-interaction wave function. The energy differences and hyperfine constants exhibit excellent overall agreement, errors in mutual separations of the bottom four levels being less than 0.025 eV. The improvements of the hfs constants over the MCDF values are striking, with four dipole and three quadrupole constants determined within the range 2.5−12.0%. The fifth dipole constant is accurate to 2 MHz but has a higher percentage error due to its tiny value. The cause of deviation of the remaining quadrupole constants seem to extend beyond the first-order theory and we provide preliminary evidence in support of our hypothesis that it would be necessary to also provide a proper description of many-body effects in the higher-lying parity-conserving states for their improved theoretical predictions.

ACKNOWLEDGMENT

We thank the Division of Chemical Sciences, Office of Energy Research, U.S. Department of Energy, Grant No. DE-FG02-92ER14282 for support of this work.

[1] D. R. Beck and D. Datta, Phys. Rev. A **48**, 182 (1993).

[2] D. Datta, Diss. Abs. Intl. **55-12B**, 5388 (1995); Ph.D. thesis, Michigan Technological University, 1994 (unpublished).

[3] L. Young, S. Hasegawa, C. Kurtz, D. Datta, and D. R. Beck, Phys. Rev. A **51**, 3534 (1995).

[4] C. Höhle, H. Hühnermann, and H. Wagner, Z. Phys. A **304**, 279 (1982).

[5] D. R. Beck, Phys. Rev. A **45**, 1399 (1992).

[6] J. Bauche, J.-F. Wyart, Z. Ben Ahmed, and K. Guidara, Z. Phys. A **304**, 285 (1982).

[7] J. P. Desclaux, D.F. Mayers, and F. O'Brien, J. Phys. B **4**, 631 (1971).

[8] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag OHG, Berlin, 1957).

[9] *Relativistic Effects in Atoms, Molecules and Solids*, Vol. 87 of *NATO Advanced Study Institute, Series B: Physics*, edited by G. L. Malli (Plenum, New York, 1983).

[10] J. P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).

[11] D. Datta and D. R. Beck, Phys. Rev. A **50**, 1107 (1994).

[12] W. C. Martin, R. Zalubas, and L. Hagan, *Atomic Energy Levels,* Natl. Bur. Stand. Ref. Data Ser. Natl. Bur. Stand. (U.S.) Circ. No. 60 (U.S. GPO, Washington, DC, 1978), the rare-earth elements.

[13] D. Datta and D. R. Beck, Phys. Rev. A **47**, 5198 (1993).

[14] G. H. Fuller and V. W. Cohen, Nucl. Data Tables A **5**, 453 (1969).