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Multiconfiguration Dirac-Fock calculations of the hyperfine structure constants and determination of the nuclear quadrupole moment of yttrium 90

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The multiconfiguration Dirac-Fock model is employed to evaluate the effects of relativity and electron correlation on the hyperfine interaction constants of the $4d5s^2\ ^2D_{3/2}$ and $^2D_{5/2}$ levels of yttrium. The wave-function expansions are obtained with the active space method, where configuration-state functions of a specific parity and J value are generated by substitutions from the reference configurations to an active set of orbitals. The active set is then increased in a systematic way, allowing the convergence of the hyperfine interaction constants to be studied. The calculated electric quadrupole hyperfine constants are used to evaluate the nuclear electric quadrupole moment of isotope 90 of yttrium, for which the value $Q=-0.125(11)$ b is found. [S1050-2947(98)06509-3]

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I. INTRODUCTION

The hyperfine structure of atomic energy levels (hereafter abbreviated to hfs) is caused by the interaction between the electrons and the electromagnetic multipole moments of the nucleus. Accurate calculations of the electronic part of the interaction permit the extraction of nuclear moments from the measured hyperfine splittings. This is especially important for quadrupole moments, which are difficult to measure directly with nuclear techniques [1]. Relativistic effects must be taken into account, even for relatively light elements [2,3], in accurate calculations of hyperfine structure. In lowest order, relativistic effects scale roughly as the square of the atomic number Z. Although perturbation theory is therefore adequate for light atoms, a fully relativistic approach is needed for heavier atoms. This is of particular importance for hyperfine structure calculations, where the results are sensitive to the form of the calculated electronic wave functions close to the nucleus [4], and the direct and indirect effects of relativity [5] are difficult to account for by quasirelativistic methods.

The atomic-beam magnetic-resonance measurements reported by Petersen and Shugart [6] provided the magnetic dipole and electric quadrupole hyperfine constants for the two lowest levels of the unstable 64-h isotope 90 of yttrium, as well as an estimate of the nuclear moments. While the accuracy of the measured hfs constants is quite good, especially with respect to the quadrupole interaction constants, which are usually much smaller and more difficult to measure, the experimental value for nuclear electric quadrupole moment Q is not quite as reliable. Their optimistic accuracy assessment did not take into account the Sternheimer shielding [7] (they acknowledged this deficiency, however), and is solely based on Schwartz [8] formulas, which provide only minimal allowance of configuration interaction. We report on the calculations of the two experimentally measured electric quadrupole hyperfine interaction constants of the $4d5s^2\ ^2D_{3/2}$ and $^2D_{5/2}$ levels of yttrium-90. The aim of this paper is to explore the effects of electron correlation on the calculated values of those two constants, and to extract the nuclear electric quadrupole moment of yttrium-90. The new version [9,10] of the GRASP [11] multiconfiguration Dirac-Fock package has been employed to generate the wave functions and the accompanying hyperfine package [12] to carry out the calculations of the expectation values.

II. THEORY

The theory was described in detail elsewhere [10–13], and only a brief description will be given here, so as to provide the background necessary for the following discussion of the computational procedures and of the results. In the multiconfiguration Dirac-Fock method [13], the relativistic atomic state function Ψ for a state labeled ΓPJM is expanded in terms of configuration state functions Φ, which are eigenfunctions of J^2, J_z, and parity P, namely

$$\Psi(\Gamma PJM)=\sum_r c_r\Phi(\gamma_r PJM). \tag{1}$$

Configuration mixing coefficients c_r are obtained through diagonalization of the Dirac-Coulomb (DC) Hamiltonian

$$H_{DC}=\sum_i c\boldsymbol{\alpha}_i\cdot\boldsymbol{p}_i+(\beta_i-1)c^2-Z/r_i+\sum_{i>j}1/r_{ij}. \tag{2}$$

The coefficients c_r, together with one-electron orbital set, provide a numerical representation of the state ΓPJM for further calculation of atomic expectation values.

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The hyperfine contribution to the Hamiltonian can be represented by a multipole expansion

$$H_{\mathrm{hfs}} = \sum_{k\geqslant 1} \mathbf{T}^{(k)} \cdot \mathbf{M}^{(k)}, \tag{3}$$

where $\mathbf{T}^{(k)}$ and $\mathbf{M}^{(k)}$ are spherical tensor operators of rank k in the electronic and nuclear space, respectively [14]. The $k=1$ term represents the magnetic dipole interaction, and the $k=2$ term the electric quadrupole interaction.

The electronic tensor operators are sums of one-particle tensor operators

$$\mathbf{T}^{(k)} = \sum_{j=1}^{N} \mathbf{t}^{(k)}(j), \quad k=1,2, \tag{4}$$

where, in atomic units,

$$\mathbf{t}^{(1)} = -i\alpha(\boldsymbol{\alpha}\cdot\mathbf{l}\;\;\mathbf{C}^{(1)})r^{-2} \tag{5}$$

and

$$\mathbf{t}^{(2)} = -\mathbf{C}^{(2)} r^{-3}. \tag{6}$$

In the formulas above, α is the fine-structure constant, $\boldsymbol{\alpha}$ is the vector of the three Dirac matrices, and $\mathbf{C}^{(k)}$ is a spherical tensor with the components related to the spherical harmonics as

$$C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}. \tag{7}$$

The magnetic dipole operator (5) represents the magnetic field due to the electrons at the site of the nucleus. The electric quadrupole operator (6) represents the electric-field gradient at the site of the nucleus.

The nuclear electric quadrupole moment Q is related to the expectation value of the nuclear tensor operator $\mathbf{M}^{(2)}$ in the state with the maximum component of the nuclear spin, $M_I = I$:

$$\langle \gamma_I II | \mathbf{M}_0^{(2)} | \gamma_I II \rangle = \frac{Q}{2}. \tag{8}$$

When the atomic state function is expanded in terms of configuration state functions [Eq. (1)], the hyperfine interaction constant B is given by

$$B_J = 2Q\left[\frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)}\right]^{1/2} \times \sum_{r,s} c_r c_s \langle \gamma_r PJ \| \mathbf{T}^{(2)} \| \gamma_s PJ \rangle. \tag{9}$$

Calculation of the matrix elements of the hyperfine operator (4) between jj-coupled configuration state functions is carried out via an expansion of the reduced matrix element $\langle \gamma_r PJ \| \mathbf{T}^{(k)} \| \gamma_s PJ \rangle$ in terms that involve single-particle orbitals only

$$\langle \gamma_r PJ \| \mathbf{T}^{(k)} \| \gamma_s PJ \rangle = \sum_{a,b} d_{ab}^{k}(rs) \langle n_a \kappa_a \| \mathbf{t}^{(k)} \| n_b \kappa_b \rangle, \tag{10}$$

where $|n_i \kappa_i\rangle$ represents a single-electron Dirac orbital.

III. METHOD OF CALCULATION

Following the example set in our previous papers [15,16] we adopted an approach [3,17–19] in which a configuration expansion set is increased in a systematic way. This makes it possible to study the convergence as well as to observe the effect of different shells on the calculated hyperfine constants. The configuration expansions were obtained with the active space method, in which configuration state functions of a particular parity and symmetry are generated by substitutions from one or more reference configurations to an active set of orbitals. The active set comprises the valence shells and several virtual shells. The set of virtual shells is systematically increased until the convergence of the hyperfine constant is obtained. In practical calculations, and especially for heavier elements, this approach is constrained by available computer storage, convergence problems, and other hardware and software limitations. The number of configurations must be kept at a manageable level, and therefore restrictions have to be imposed on the allowed substitutions, so that the most important electron correlation effects are captured.

In first-order perturbation theory, only single substitutions contribute to the hfs energy correction [20,21], so they usually comprise the dominant part of the hfs energy. On the other hand, double substitutions dominate energetically over the valence correlation corrections and, consequently, the virtual orbitals obtained in fully optimized and fully correlated variational calculations are optimized predominantly through the effects of double substitutions on the total energy. Therefore in the hfs calculations it is important that the virtual space also be sufficiently saturated with orbitals optimized for single substitutions [22,23]. Although large-scale fully relativistic calculations are now feasible, and can give fairly accurate results [24,25], the large-scale multiconfiguration calculations are still very expensive computationally. The complete active space approach is unattainable, except perhaps for very light elements [26,27], and a strategy is needed to ensure that all important contributions are included in more limited expansions. Bearing this in mind, we adopted a scheme [28], in which the virtual orbital space is optimized for single substitutions, while the effects of double substitutions are accounted for through post-self-consistent-field configuration interaction calculations. All calculations were done with the nucleus modeled as a variable-density spherical ball, where a two-parameter Fermi distribution [11]

$$\rho(r) = \frac{\rho_0}{1+e^{(r-c)/a}} \tag{11}$$

was employed to approximate the charge distribution. The parameter c is the *half-charge radius*, and a is related to the *skin thickness*, the interval across which the nuclear charge density falls from near one to near zero.

TABLE I. Quadrupole moment Q as a function of different configuration expansions for the $4d5s^2\ {}^2D_{3/2}$ state of yttrium-90. The notation $2spdf1g$ in the third column refers to substitutions to virtual space constructed from two orbitals of each of the s, p, d, and f symmetries, and one orbital of g symmetry.

CSF	From	To	Type	Q (b)
1	$4d5s^2$	—	—	−0.1368
45	$4pd5s$	$1spdf$	S	−0.2259
245	$3pd4spd5s$	$2spdf$	S	−0.1401
273	$3pd4spd5s$	$2spdf1g$	S	−0.1396
1028	$3pd4sp(4d5s^2+5s5p^2)$	$2spdf1g$	S	−0.1309
440	$3spd4spd5s$	$3spdf1g$	S	−0.1264
472	$3spd4spd5s$	$3spdf2g$	S	−0.1276
584	$2sp3spd4spd5s$	$3spdf1g$	S	−0.1271
864	$2sp3spd4spd5s$	$4spdf3g1h$	S	−0.1264
1093	$2sp3spd4spd5s$	$5spdf4g1h$	S	−0.1229
1286	$2sp3spd4spd5s$	$6spdf4g1h$	S	−0.1235
1479	$2sp3spd4spd5s$	$7spdf4g1h$	S	−0.1233
1580	$1s2sp3spd4spd5s$	$7spdf4g1h$	S	−0.1233
5008	$1s2sp3spd4spd5s$	$7spdf4g1h$	S	
	$4pd5s$	$1spdf$	D	−0.1130
13 519	$1s2sp3spd4spd5s$	$7spdf4g1h$	S	
	$3pd4spd5s$	$2spdf$	D	−0.1118

The generation of the wave functions followed essentially the scheme described in our previous papers [15,16]. First, the spectroscopic orbitals required to form a reference wave function were obtained in a single configuration calculation, with full relaxation. Only the level involved was represented, and the resulting reference wave function was used as a starting point for further calculations. The generation of further layers of virtual space followed in steps, one layer at each step, with all previous configuration expansions included. All virtual orbitals were generated with the expansions formed by single substitutions from the reference configuration. To obtain converged values of the hyperfine constants within the single substitutional approach, typically a few thousand configuration state functions are needed, depending on the expected precision. The structure of virtual orbital space is best understood by inspection of the first four columns of one of Tables I and II. The single (S) substitutions promote the electrons from the spectroscopic orbitals listed in column 2 to the virtual space presented in column 3, giving the total number of configurations listed in column 1. In column 3 the notation $2spdf1g$ means substitutions to virtual space constructed from two orbitals of each of the s, p, d, and f

TABLE II. Quadrupole moment Q as a function of different configuration expansions for the $4d5s^2\ {}^2D_{5/2}$ state of yttrium-90. The notation $2spdf1g$ in the third column refers to substitutions to virtual space constructed from two orbitals of each of the s, p, d, and f symmetries, and one orbital of g symmetry.

CSF	From	To	Type	Q (b)
1	$4d5s^2$	—	—	−0.1384
49	$4pd5s$	$1spdf$	S	−0.2145
309	$3pd4spd5s$	$2spdf1g$	S	−0.1413
334	$3spd4spd5s$	$2spdf1g$	S	−0.1414
1265	$3pd4sp(4d5s^2+5s5p^2)$	$2spdf1g$	S	−0.1332
491	$3spd4spd5s$	$3spdf1g$	S	−0.12526
540	$3spd4spd5s$	$3spdf2g$	S	−0.12529
650	$2sp3spd4spd5s$	$3spdf1g$	S	−0.1257
1007	$2sp3spd4spd5s$	$4spdf3g1h$	S	−0.1251
1272	$2sp3spd4spd5s$	$5spdf4g1h$	S	−0.1220
1481	$2sp3spd4spd5s$	$6spdf4g1h$	S	−0.1256
1690	$2sp3spd4spd5s$	$7spdf4g1h$	S	−0.1257
1991	$1s2sp3spd4spd5s$	$7spdf4g1h$	S	−0.1257
5799	$1s2sp3spd4spd5s$	$7spdf4g1h$	S	
	$4pd5s$	$1spdf$	D	−0.1181
15 782	$1s2sp3spd4spd5s$	$7spdf4g1h$	S	
	$3pd4spd5s$	$2spdf$	D	−0.1160

symmetries, and one orbital of g symmetry. The optimal level form of the variational expression [11] has been applied in all variational calculations presented below. The procedure employed to generate the wave functions was very similar for both levels considered in this study. Due to different angular symmetry, the configuration expansions for the $4d5s^2\ ^2D_{5/2}$ state are larger by about 10%, but the overall dependence of the calculated value of Q on configuration expansions is very much the same in both cases. After initial oscillations, the values B began to saturate reasonably quickly. When they reached the three-digit precision, the procedure has been stopped, since the experimental values of hfs constants B are known to about the same accuracy. The contributions of core orbitals to the computed values of Q have been controlled both during the process of building the virtual space, as well as in the series of post-self-consistent-field configuration interaction calculations. As demonstrated by the comparison of lines 2 and 3 of Tables I and II, the contributions from $n=3$ are expected to be quite large, and the effects arising from the $n=2$ shell (lines 6 and 8) are also quite significant, affecting the third digit of the value of Q. On the other hand, the effect of the opening of the $1s$ orbital is much smaller, as can be seen from the comparison of line 13 (where a configuration-interaction calculation, including the substitutions from $1s$ shell, is reported) and line 12. This turned out to be fifth-digit effect, well beyond our targetted precision. The importance of virtual orbitals with high angular momentum values has also been monitored during the calculations, and it appears that there are no effects beyond the g symmetry, which would contribute at the present level of accuracy (inspection of lines 6 and 7 of Table I shows that the effect of adding a second orbital of g symmetry is of the order of 1% for the $^2D_{3/2}$ state; in the case of the $^2D_{5/2}$ state, it is even smaller). The reader is referred to our previous paper [16] and to published computer codes [10,12] for the numerical details of the computational procedures necessary to generate wave functions, and subsequently compute the observables.

IV. ELECTRON CORRELATION EFFECTS

As described in Sec. III, the present study aims at recovering the electron correlation effects arising from single substitutions, since they dominate the hyperfine energy. The virtual orbital space was formed by single substitutions from a single-configuration reference wave function. For a system as heavy as yttrium, this is the only feasible approach permitted by the capabilities of contemporary computers. In order to estimate the corrections arising from dominant electron correlation effects not accounted for within this model, we performed a series of configuration-interaction calculations. First, the quality of the reference wave function has been tested by the configuration-interaction calculation, in which the single-configuration reference wave function $4d5s^2$ has been replaced by a two-configuration reference wave function of the form $4d5s^2+5s5p^2$, since the $5s5p^2$ configuration is expected to be the dominant contributor to the electron correlation effects arising from the valence electron interactions. The calculations performed with the double-configuration reference wave function are presented in line 5 of Tables I and II. The comparison with the previous line demonstrates that the effect is of the order of 6%. As a second test, we performed two large-scale configuration-interaction calculations, involving the most important double substitutions. As can be seen from the last two entries in the Tables I and II, the dominant contribution comes from double substitutions involving the outermost electron shells. Also, the overall effect of the double substitutions is quite large, on the order of 10%. This matter will be discussed further in Sec. V.

V. RESULTS AND DISCUSSION

It is interesting to note how close the results for the $^2D_{5/2}$ level match those for $^2D_{3/2}$. Both the largest variational results and the configuration-interaction values differ very little from one level to the other. It would be tempting to assume that this agreement was an indication of the consistency of the two calculations, and to present the configuration-interaction values as the final outcome of this study. It should be stressed, though, that all configuration-interaction calculations have been performed with the orbital basis formed from virtual orbitals generated in the single-substitution phase of the project. The orbitals have been optimized for single substitutions, and therefore they are not necessarily optimal for double-substitution calculations. In the single-substitution model the configuration expansion is certainly not sufficiently saturated, which is the main source of error in the present calculations. The configuration-interaction calculations presented in line 5 and in the last two entries in both Tables I and II give us some indication of how large are the effects of double- and higher order substitutions. Therefore we adopted a more conservative approach, which treats the configuration-interaction calculations only as means to estimate the error. Any reasonable statistical error analysis would certainly require more than two values, so the departure of the configuration-interaction values from the variational ones can only serve as a very crude estimate of the error of the final value, which we assess as $Q=-0.125(11)$ b. It is worth noting that the semiempirical result of Petersen and Shugart [6], $Q=-0.155(3)$, is 11% away even from the single-configuration Dirac-Fock values of Q, and also that it is outside the relatively large (10%) error bars of our final value, although all of them are based on the same experimentally determined quadrupole constants B. The availability of hfs measurements for other levels in the Y-90 spectrum would certainly be welcome, as a vehicle to improve the accuracy of our calculations and to verify the above disagreement.

VI. CONCLUSIONS

We have performed large-scale multiconfiguration Dirac-Fock calculations of electric quadrupole hyperfine structure constants for the $4d5s^2\ ^2D_{3/2}$ and $^2D_{5/2}$ levels of Y-90. The single-substitution model has been employed to account for Sternheimer correction. The nuclear electric quadrupole moment Q has been extracted from two experimentally known B constants. The resulting value of $Q=-0.125(11)$ b is 20% smaller than previously computed semiempirical [6] value $Q=-0.155(3)$.

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