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Large-scale multiconfiguration Hartree-Fock and configuration-interaction calculations of the transition probability and hyperfine structures in the sodium resonance transition

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Results from large-scale multiconfiguration Hartree-Fock (MCHF) and configuration-interaction (CI) calculations of the transition probability and hyperfine structures in the sodium $3s\ ^2S-3p\ ^2P$ resonance transition are presented. In the calculations the orbital sets of the initial and final state wave functions were not restricted to be the same, but were optimized independently. The evaluation of the transition matrix elements was done using a technique where the two orbital sets are transformed so as to become biorthonormal, in which case standard Racah algebra can be used. Three-particle effects were taken into account in the CI calculations and were found to be important for the hyperfine structures, but less important for the transition probability. The calculated transition probability is in perfect agreement with the most recent experimental values, thus resolving the long-standing disagreement between theory and experiment. Also the $3s\ ^2S_{1/2}$ and $3p\ ^2P_{1/2,3/2}$ hyperfine interaction constants are in very good agreement with available experimental values. [S1050-2947(96)07806-7]

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I. INTRODUCTION

Recent progress in computational techniques, together with today's powerful computers, has made it possible to calculate hyperfine structures and isotope shifts in light atoms with very high accuracy. See, for example, [1–7] and references therein. For these properties a great number of accurate experimental values are available, and a detailed comparison shows that in favorable cases theoretical and experimental values agree to within a few parts in a thousand.

By contrast, there has been a seemingly persistent disagreement between the most accurate theoretical and experimental values for transition probabilities. Well known examples of this are the resonance lines in lithium and sodium, for which the theoretical values of the transition parameters disagree with the most accurate experimental values at the percent level. For a recent review see Brage *et al.* [8].

This disagreement between the theoretical and experimental values is especially severe for lithium, a system simple enough allowing for an almost exact theoretical treatment with a number of different methods. Considering the fact that all the theoretical values agree perfectly, with the exception of a recent quantum Monte Carlo calculation [9], but are well outside the error bars of the fast-beam laser measurement of Gaupp *et al.* [11], one might be inclined to believe that the latter are too small. This belief is supported by a new fast-beam laser measurement [10] as well as by a measurement using photoassociative spectroscopy on ultracold lithium [12]. Both these quite different measurements give values which agree well with the theoretical values.

For sodium the situation is different. Here accurate calculations of transition parameters, such as the multiplet strength, have remained difficult due to orthogonality restrictions. To evaluate transition matrix elements using standard Racah-algebra techniques the two states involved in the transition have to be described by the same orbital set [13] (see also Froese Fischer *et al.* [14], who have relaxed the orthogonality condition slightly). A high-quality wave function, however, demands orbitals optimized for the specific electronic state, and it is usually not possible to obtain an accurate description when the same orbital set is used for two different states. This problem can be overcome using a biorthonormal orbital transformation technique [15] that has been extended recently to symmetry adapted configuration state expansions [16], and it is now possible to perform large-scale transition calculations where the orbital sets of the two wave functions are not assumed to be the same, but can be optimized independently.

In an effort to resolve the disagreement between the experimental and theoretical transition parameters for sodium, we performed large-scale multiconfiguration Hartree-Fock (MCHF) and configuration-interaction (CI) calculations for the $3s\ ^2S$ and $3p\ ^2P$ terms using the biorthonormal transformation technique to evaluate the transition matrix elements. As an additional test on the quality of the wave functions, the hyperfine interaction constants were calculated for all the states involved in the transition.

Three-particle effects were taken into account in the CI calculations to yield a deeper understanding of correlation in the alkali-metal atoms. Whereas these effects have been included in previous calculations of the hyperfine structure in the sodium ground state [5], giving surprisingly large contributions, the importance for the transition parameters are less well known.

The major part of the calculations reported here were performed on a DEC 5100 workstation with 32 Mb internal memory using different modules of the MCHF atomic structure package of Froese Fischer [17–21], modified for large scale computation. The largest calculations for the $3p\ ^2P$ term were performed on an IBM SP-2 at Kingston, using a distributed memory version of the atomic structure package [22].

II. THEORY

A. MCHF

In the nonrelativistic MCHF approach [23] the wave function ψ for a state labeled γLS, where γ represents the configuration and any other quantum numbers required to specify the state, is expanded in terms of configuration state functions (CSF's) with the same LS term.

$$\psi(\gamma LS)=\sum_j c_j \Phi(\gamma_j LS). \tag{1}$$

The configuration state functions Φ are antisymmetrized linear combinations of products of spin-orbitals,

$$\phi_{nlm_lm_s}=\frac{1}{r}P_{nl}(r)Y_{lm_l}(\theta,\varphi)\xi_{m_s}(\sigma), \tag{2}$$

where the radial functions $P_{nl}(r)$ are represented by their numerical values at a number of grid points. The radial functions are required to be orthonormal within each l-symmetry,

$$\int_0^\infty P_{n'l}(r)P_{nl}(r)dr=\delta_{n'n}. \tag{3}$$

In the multiconfiguration self-consistent field (MC-SCF) procedure both the orbitals and the expansion coefficients are optimized to self-consistency.

B. CI

Once a set of radial orbitals has been obtained, a configuration interaction (CI) calculation can be performed. In a CI calculation the wave function is expanded in configuration state functions, but now only the expansion coefficients are to be determined. This is done by diagonalizing the Hamiltonian matrix. For small expansions standard routines from numerical libraries can be used, but for larger expansions these routines become inefficient. Instead, the iterative Davidson method [24] can be used to determine a restricted number of the lowest eigenvalues and eigenvectors. Using a sparse matrix representation [25], where only nonzero matrix elements are saved, large expansions can be used, the limit being set by the available disk space.

C. Hyperfine structure

The hyperfine structure is due to the interaction between the electrons and the nuclear magnetic dipole and electric quadrupole moments. The interaction couples the nuclear, **I**, and electronic, **J**, angular momenta to a total momentum $\mathbf{F}=\mathbf{I}+\mathbf{J}$, and leads to a splitting of the fine structure levels. The splitting is often given in terms of the magnetic dipole and electric quadrupole interaction constants A_J and B_J,

$$A_J=\frac{\mu_I}{I}\frac{1}{[J(J+1)(2J+1)]^{1/2}}\langle\gamma_J J\|\mathbf{T}^{(1)}\|\gamma_J J\rangle, \tag{4}$$

$$B_J=2Q\left[\frac{J(2J-1)}{(J+1)(2J+1)(2J+3)}\right]^{1/2}\langle\gamma_J J\|\mathbf{T}^{(2)}\|\gamma_J J\rangle, \tag{5}$$

where I is the nuclear spin, μ_I the nuclear magnetic dipole moment, and Q the nuclear quadrupole moment. For ^{23}Na the values of the first two parameters are $I=3/2$ and $\mu_I=2.217\,655\,6\mu_N$ [26]. The electronic tensor operators $\mathbf{T}^{(1)}$ and $\mathbf{T}^{(2)}$ are given by

$$\mathbf{T}^{(1)}=\frac{\alpha^2}{2}\sum_{i=1}^{N}\{2\mathbf{l}^{(1)}(i)r_i^{-3}-g_s\sqrt{10}[\mathbf{C}^{(2)}(i)\times\mathbf{s}^{(1)}(i)]^{(1)}r_i^{-3} + g_s\tfrac{8}{3}\pi\delta(\mathbf{r}_i)\mathbf{s}^{(1)}(i)\} \tag{6}$$

and

$$\mathbf{T}^{(2)}=-\sum_{i=1}^{N}\mathbf{C}^{(2)}(i)r_i^{-3}, \tag{7}$$

where $g_s=2.002\,319\,3$ is the electron spin g factor, $\mathbf{l}^{(1)}$ and $\mathbf{s}^{(1)}$ are, respectively, the orbital and spin angular momentum operators, and $\mathbf{C}^{(k)}$ is a spherical tensor of rank k with the components related to the spherical harmonics as

$$C_q^{(k)}=\sqrt{\frac{4\pi}{2k+1}}Y_{kq}. \tag{8}$$

D. Multiplet strength

The multiplet strength for the transition between two terms $\gamma'L'S'$ and γLS in the length form can be written [27]

$$S_l=\left|\left\langle\gamma LS\left\|\sum_{i=1}^{N}r_i\mathbf{C}^{(1)}(i)\right\|\gamma'L'S'\right\rangle\right|^2. \tag{9}$$

To obtain a value of the multiplet strength, the transition matrix element must be evaluated,

$$\left\langle\gamma LS\left\|\sum_{i=1}^{N}r_i\mathbf{C}^{(1)}(i)\right\|\gamma'L'S'\right\rangle. \tag{10}$$

In cases where both the initial and final states are given by configuration state expansions

$$\psi(\gamma' L' S') = \sum_j c'_j \Phi(\gamma'_j L' S'), \qquad (11)$$

$$\psi(\gamma LS) = \sum_k c_k \Phi(\gamma_k LS), \qquad (12)$$

the transition matrix elements can be written

$$\left\langle \gamma LS \left\| \sum_{i=1}^{N} r_i \mathbf{C}^{(1)}(i) \right\| \gamma' L' S' \right\rangle = \sum_{k,j} c_k c'_j \left\langle \Phi(\gamma_k LS) \left\| \sum_{i=1}^{N} r_i \mathbf{C}^{(1)}(i) \right\| \Phi(\gamma'_j L' S') \right\rangle \qquad (13)$$

and the evaluation reduces to the evaluation of matrix elements between arbitrarily LS coupled CSF's

$$\left\langle \Phi(\gamma_k LS) \left\| \sum_{i=1}^{N} r_i \mathbf{C}^{(1)}(i) \right\| \Phi(\gamma'_j L' S') \right\rangle. \qquad (14)$$

This can be done with standard Racah-algebra assuming that both left and right CSF's are formed from the *same* orthonormal set of spin-orbitals [13]. This is a very severe restriction, since a high-quality wave function requires that orbitals be optimized for a specific electronic state. Recently, however, it has been shown [16] that for very general configuration expansions, where the initial and final states are described by different orbital sets, it is possible to change the wave function representation of the two states in such a way that the standard Racah-algebra can be used for the evaluation of the matrix elements in the new representation. The procedure for the calculation of the transition matrix element can be summarized as follows.

(i) Perform MCHF or CI calculations for the initial and the final state where the one-electron orbital sets of the two wave functions ($\{\phi_i\}$ and $\{\phi'_i\}$) are *not* assumed to be the same.

(ii) Change the wave function representation by transforming the two orbital sets

$$\{\phi_i\} \rightarrow \{\tilde{\phi}_i\}, \quad \{\phi'_i\} \rightarrow \{\tilde{\phi}'_i\}$$

to a biorthonormal basis, i.e., $\langle \tilde{\phi}_i | \tilde{\phi}'_j \rangle = \delta_{ij}$. The orbital transformation in effect changes the CSF's and we have

$$\{\Phi(\gamma_k LS)\} \rightarrow \{\tilde{\Phi}(\gamma_k LS)\}, \quad \{\Phi(\gamma'_j L' S')\} \rightarrow \{\tilde{\Phi}(\gamma'_j L' S')\}.$$

The orbital transformation is followed by a counter-transformation of the CI expansion coefficients

$$\{c_k\} \rightarrow \{\tilde{c}_k\}, \quad \{c'_j\} \rightarrow \{\tilde{c}'_j\}$$

so as to leave the total wave functions invariant, i.e.,

$$\psi(\gamma LS) = \sum_k c_k \Phi(\gamma_k LS) \equiv \sum_k \tilde{c}_k \tilde{\Phi}(\gamma_k LS)$$

and

$$\psi(\gamma' L' S') = \sum_j c'_j \Phi(\gamma'_j L' S') \equiv \sum_j \tilde{c}'_j \tilde{\Phi}(\gamma'_j L' S').$$

(iii) Calculate the transition matrix element with the transformed wave functions for which now the standard Racah-algebra can be used:

$$\left\langle \gamma LS \left\| \sum_{i=1}^{N} r_i \mathbf{C}^{(1)}(i) \right\| \gamma' L' S' \right\rangle = \sum_{k,j} \tilde{c}_k \tilde{c}'_j \left\langle \tilde{\Phi}(\gamma_k LS) \left\| \sum_{i=1}^{N} r_i \mathbf{C}^{(1)}(i) \right\| \tilde{\Phi}(\gamma'_j L' S') \right\rangle. \qquad (15)$$

The details of the transformation are discussed in [15,16].

III. CALCULATIONS

A. Selection of configuration expansions

The configuration expansions for the MCHF and CI calculations were obtained with the active space method [29,30], where CSF's of a specified parity and LS symmetry are generated by excitations from one or more reference configurations to an active set of orbitals. In order to study the convergence of the calculated multiplet strength and hyperfine interaction constants, the active set was increased in a systematic way leading to consecutively larger configuration expansions. The notation of the active set of orbitals follows the conventions used in quantum chemistry where, for example, the set $3s2p1d$ contains three s orbitals, two p orbitals, and one d orbital. Except for the reference configuration, principal quantum numbers have no significance other than defining the order in which the orbitals are introduced.

In the MCHF method the radial parts of the orbitals in the active set are obtained by minimizing the total energy for a certain configuration expansion. The shape and spatial location of the resulting orbitals do, of course, strongly depend on how this configuration expansion is chosen. If, for the $3s\ ^2S$ and $3p\ ^2P$ terms in sodium, the configuration expansion is generated by allowing all single (S) and double (D) excitations from the reference configuration to the active set in order to account for the energetically dominating pair correlation effects, the first correlation orbitals in the active set will be strongly contracted. These strongly contracted orbitals describe mainly core-core correlation effects. As the active set is increased, the core-core correlation effects gradually saturate, and the new orbitals tend to be localized between the $2p$ core shell and the valence shell, accounting for the core-valence effects. Since core-core effects are energetically much more important than core-valence effects, a large number of orbitals is needed before the latter effects are described in a proper way. The fundamental problem with the MCHF method, and variational methods in general, is that the expectation values of many operators describing measurable physical quantities have a different dependence on the correlation effects than the total energy. The expectation values of the hyperfine and transition operators, for example, are more sensitive to core-valence effects than to core-core effects. Thus, to obtain reliable expectation values of these operators, one has to ensure that the generated active

TABLE I. The interaction constant $A_{1/2}$, the total energy, and the number of CSF's for the $3s\ ^2S_{1/2}$ state in ^{23}Na from core-valence and core-core MCHF calculations and from CI calculations including triple-excitations. The configuration expansions for the core-valence calculations were generated by allowing all SD excitations from $1s^22s^22p^63s$ to the active set with the restriction that there should be no more than one excitation from the core. The configuration expansions for the core-core calculations were obtained by allowing all SD excitations from $1s^22s^22p^63s$ to the active set without restrictions. The expansions for the CI calculations were obtained by adding CSF's generated by T excitations to the active sets to the CSF's generated by SD excitations from $1s^22s^22p^63s$ to the $10s9p8d7f6g5h4i$ active set. The orbital optimization procedures are described in the text.

Active set	$A_{1/2}$ (MHz)	Energy (a.u.)	Number of CSF's
HF	626.2	-161.858 912	1
MCHF core-valence			
$3s2p1d$	683.6	-161.863 313	11
$4s3p2d1f$	843.2	-161.866 122	48
$5s4p3d2f1g$	884.2	-161.866 771	119
$6s5p4d3f2g1h$	907.6	-161.866 997	232
$7s6p5d4f3g2h1i$	927.6	-161.867 099	395
$8s7p6d5f4g3h2i$	928.1	-161.867 145	610
CI core-core:			
$8s7p6d5f4g3h2i$	868.8	-162.223 684	3 362
MCHF core-core:			
$9s8p7d6f5g4h3i$	865.0	-162.233 637	4 875
$10s9p8d7f6g5h4i$	865.4	-162.236 676	6 687
$11s10p9d8f7g6h5i$	865.7	-162.237 890	8 798
CI core-core + triple-exc.			
SD$[10s9p8d7f6g5h4i]$			
$\cup T[4s3p2d1f]$	868.4	-162.238 239	9 911
$\cup T[5s4p3d2f1g]$	871.0	-162.239 969	24 078
$\cup T[6s5p4d3f2g1h]$	870.3	-162.240 734	66 394

set of orbitals is flexible enough to describe also the core-valence effects.

To ensure a good description of the core-valence effects in the present calculation, orbitals were explicitly targeted to describe these effects. This was done by taking into account only single excitations from the $1s^22s^22p^6$ core to the active set. In this way the core-core effects were left out, and the correlation orbitals were forced to describe the energetically less important core-valence effects. Once the core-valence correlation effects saturated, the active set was extended to include contracted orbitals that are necessary to describe the core-core correlation effects.

B. The $3s\ ^2S$ term

As a starting point, a Hartree-Fock (HF) calculation was performed for the $1s^22s^22p^63s\ ^2S$ reference configuration. Then a sequence of MCHF calculations were performed for expansions generated by SD excitations from $1s^22s^22p^63s$ to the active set with the restriction that at most single excitations were allowed from the core. As discussed above, these expansions mainly describe core-valence effects and result in an orbital basis largely localized between the $3s$ valence shell and the $2p$ core shell. In these calculations the core orbitals were kept fixed whereas the rest of the orbitals were optimized simultaneously. In the first part of Table I, the hyperfine interaction constant, the total energy, and number of generated configuration state functions are reported as functions of the active set of orbitals. As can be seen from the table, the convergence of the hyperfine interaction constant with respect to the active set is rather slow, but for the $8s7p6d5f4g3h2i$ active set the core-valence limit seems to have been reached.

To investigate the effect of core-core correlation, a CI calculation was performed for the configuration expansion generated by allowing all SD excitation to the $8s7p6d5f4g3h2i$ active set. As can be seen from the first line in the middle part of Table I, the included core-core correlation decreases the hyperfine interaction constant by almost 60 MHz. Analyzing the contributions to the hyperfine interaction constant from the CSF's in the CI expansion, it can be seen that the effect of the core-core correlation on this property is mainly indirect. Being not directly coupled with the dominant reference configuration through the hyperfine operator, the CSF's describing core-core correlation play their role through their relatively large expansion weights due to their important contribution to the total energy. When these core-core correlation components are added, the expansion weights of the CSF's describing core-valence correlation decrease, lowering the value of the hyperfine interaction constant. For a more detailed investigation of these effects in the case of the first row atoms, see Ref. [31]. To ensure convergence of the core-core effects, the active set was in-

TABLE II. The expectation values of the radius for some of the radial orbitals in the active set used for the $3s\ ^2S$ term.

Reference orbitals	$\langle r\rangle$	Core-valence orbitals	$\langle r\rangle$	Core-core orbitals	$\langle r\rangle$
$1s$	0.14286	$4s$	1.91634	$9s$	0.31546
$2s$	0.77907	$4p$	2.03202	$9p$	0.35959
$2p$	0.79849	$4d$	1.87848	$9d$	0.32852
$3s$	4.07115	$4f$	1.77163	$9f$	0.35207

creased, and additional MCHF calculations were performed for expansions generated by SD excitations to the active set. In these calculations the orbitals from the previous core-valence calculations ($8s7p6d5f4g3h2i$) were fixed and only the new orbitals were optimized. As can be seen from the table, the additional core-core effects have only a small influence on the hyperfine interaction constant, which seems to be well converged for the $10s9p8d7f6g5h4i$ active set.

The added orbitals describing core-core effects are strongly contracted compared with the orbitals describing core-valence effects. To illustrate this, the radial expectation values

$$\langle r\rangle = \int_0^\infty r P_{nl}^2(r)\,dr \tag{16}$$

of the reference orbitals and some of the correlation orbitals are compared in Table II.

It is well known that three-particle effects are important for the hyperfine structure [6]. To account for these, a set of CI calculations was performed using the orbital set of the $10s9p8d7f6g5h4i$ MCHF core-core calculation, for expansions where configurations generated by triple (T) excitations from $1s^22s^22p^63s$ to systematically larger active sets were added to the configurations generated by SD excitations from $1s^22s^22p^63s$ to the $10s9p8d7f6g5h4i$ active set. This addition is symbolized by the union ($\cup$) of the two CSF sets in Table I. As can be seen from the lower part of Table I, the effect of the triple excitations is to increase the hyperfine interaction constants. Previous tests [28] showed that four-particle effects increase the value of the hyperfine interaction constant. This increase, however, is small (less than 2 MHz), and four-particle effects have therefore been neglected in all the CI calculations.

TABLE III. The interaction constants A_J and B_J, the total energy, and the number of CSF's for the $3p\ ^2P_{1/2,3/2}$ states in ^{23}Na from core-valence and core-core MCHF calculations and from CI calculations including triple excitations. The configuration expansions for the core-valence calculations were generated by allowing all SD excitations from $1s^22s^22p^63p$ to the active set with the restriction that there should be no more than one excitation from the core. The configuration expansions for the core-core calculations were obtained by allowing all SD excitations from $1s^22s^22p^63p$ to the active set without restrictions. The expansions for the CI calculations were obtained by adding CSF's generated by T excitations to the active sets to the CSF's generated by SD excitations from $1s^22s^22p^63p$ to the $10s9p8d7f6g5h4i$ active set. The orbital optimization procedures are described in the text.

Active set	$A_{1/2}$ (MHz)	$A_{3/2}$ (MHz)	$B_{3/2}/Q$ (MHz/b)	Energy	Number of CSF's
HF	63.66	12.72	15.91	-161.786 408	1
MCHF core-valence					
$3s2p1d$	66.94	11.82	16.20	-161.786 912	18
$4s3p2d1f$	94.69	21.64	28.90	-161.788 795	85
$5s4p3d2f1g$	96.67	21.67	27.88	-161.789 184	221
$6s5p4d3f2g1h$	100.44	20.73	28.63	-161.789 317	444
$7s6p5d4f3g2h1i$	101.13	20.54	28.70	-161.789 366	772
$8s7p6d5f4g3h2i$	101.57	20.56	28.52	-161.789 385	1 206
CI core-core:					
$8s7p6d5f4g3h2i$	91.89	18.16	25.80	-162.140 285	16 818
MCHF core-core:					
$9s8p7d6f5g4h3i$	92.38	18.29	25.27	-162.156 406	24 733
$10s9p8d7f6g5h4i$	92.33	18.29	25.23	-162.159 742	34 247
CI core-core + triple-exc.					
SD[$10s9p8d7f6g5h4i$]					
$\cup T[4s3p2d1f]$	92.53	18.49	25.37	-162.160 640	50 864
$\cup T[5s4p3d2f1g]$	93.16	18.74	25.67	-162.162 173	135 060

C. The $3p\ ^2P$ term

The calculations for the $3p\ ^2P$ term were performed in the same way as for the $3s\ ^2S$ term. In the first part of Table III, the hyperfine interaction constants, the total energy, and number of generated configuration state functions are reported as functions of the increasing active set. For the $3p\ ^2P$ term the core-valence limit of the hyperfine interaction parameters is reached already for the $7s6p5d4f3g2h1i$ active set, but, in order to be consistent with the previous calculations for the $3s\ ^2S$ term, the core-valence effects were evaluated also for the $8s7p6d5f4g3h2i$ active set. As for the $3s\ ^2S$ term, the effect of the core-core correlation is to decrease the hyperfine interaction constants. This decrease is even more pronounced for $3p\ ^2P$ than for $3s\ ^2S$ and is of the order of 10% for all the hyperfine interaction constants. The additional core-core effects, included as the active set is increased, are of little importance, and the core-core effects are very well converged for the $10s9p8d7f6g5h4i$ active set.

To account for three-particle effects, a set of CI calculations was performed for expansions where configurations generated by triple excitations from $1s^22s^22p^63p$ to systematically larger active sets were added to the configurations generated by SD excitations from $1s^22s^22p^63p$ to the $10s9p8d7f6g5h4i$ active set, using the orbital set of the largest MCHF core-core calculation. Due to the ^2P symmetry the number of CSF's in the CI expansion grows very rapidly with the increasing active set, and it was not possible to extend the calculations by allowing triple excitations to the $6s5p4d3f2g1h$ active set. This is unfortunate since the hyperfine interaction constants are not properly converged with respect to three-particle effects. However, a comparison with the convergence trend of the hyperfine interaction constant for the $3s\ ^2S_{1/2}$ state suggests that the remaining three-particle effects are small. One should note, however, that the three-particle effects are relatively more important for the $3p\ ^2P_{1/2,3/2}$ states than for the $3s\ ^2S_{1/2}$ state.

D. The $3s\ ^2S \rightarrow 3p\ ^2P$ multiplet strength

The $3s\ ^2S \rightarrow 3p\ ^2P$ multiplet strength was evaluated from the generated MCHF and CI wave functions. The multiplet strength and the transition energy are shown in Table IV as functions of the active set of orbitals.

The multiplet strength and hyperfine interaction constants have different dependencies on the correlation effects, and it is interesting to compare the convergence trends. Part of the differences in the latter can be explained by the different radial scaling of the corresponding operators. The core-valence correlation leads to a contraction of the valence orbital. Since the hyperfine operators scale as r^{-3}, the effect of this contraction is to increase the hyperfine interaction constants. The behavior for the multiplet strength is the opposite. Since the transition operator scales like r, the effect of the contraction is to decrease the multiplet strength. The size of this effect can be seen in the first part of Table IV, where the multiplet strength and the energy difference between the initial and final states for the transition are shown as functions of the active set of orbitals for the core-valence expansions.

As can be seen from the middle part of Table IV, the effect of the core-core correlation is to increase the multiplet strength, that is, to counteract the effect of the core-valence correlation. This behavior was also found for the hyperfine interaction constants.

TABLE IV. The multiplet strength in the length form and the energy difference between the initial and final states for the $3s\ ^2S \rightarrow 3p\ ^2P$ transition from core-valence and core-core MCHF calculations and from CI calculations including triple excitations. The active sets are the same for the initial and final states.

Active set	S_l	ΔE (cm^{-1})
HF	40.82	15 913
MCHF core-valence		
$3s2p1d$	38.41	16 768
$4s3p2d1f$	37.20	16 971
$5s4p3d2f1g$	36.97	17 028
$6s5p4d3f2g1h$	36.89	17 048
$7s6p5d4f3g2h1i$	36.86	17 060
$8s7p6d5f4g3h2i$	36.84	17 066
CI core-core:		
$8s7p6d5f4g3h2i$	37.20	18 304
MCHF core-core:		
$9s8p7d6f5g4h3i$	37.40	16 950
$10s9p8d7f6g5h4i$	37.40	16 885
CI core-core + triple-exc.		
SD$[10s9p8d7f6g5h4i]$		
$\cup T[4s3p2d1f]$	37.34	17 031
$\cup T[5s4p3d2f1g]$	37.35	17 074
Estimated [a]		16 933.5

[a] Estimated nonrelativistic transition energy of Ref. [32].

As for the hyperfine interaction constants, the additional core-core effects, included as the active set is increased, are of little importance, and the core-core effects seem to be very well converged for the $10s9p8d7f6g5h4i$ active set. Finally, the effect of the triple-excitations, as can be seen from the last part of the table, is to decrease the multiplet strength. This decrease is, however, small compared with the corresponding increase of the hyperfine interaction constants.

Whereas the hyperfine interaction constants and the multiplet strength are well converged with respect to the different correlation effects, the transition energy is not. As is seen from Table IV, the transition energy is well converged with respect to the core-valence correlation. However, when the core-core correlation is introduced the transition energy changes dramatically, and the active set describing the core-core effects must be increased further in order to get a converged value of the transition energy. Looking at the last part of Table IV it is seen that three-particle effects have a large influence on the transition energy. The transition energy is clearly not converged with respect to these effects, and also in this case it is necessary to increase the active set to which excitations are done in order to get a converged value. In addition to the lacking convergence of the transition energy with respect to the core-core and three-particle effects, the neglected four-particle effects are expected to be of importance. Therefore, no meaningful comparison with the esti-

TABLE V. The interaction constant $A_{1/2}$ (in MHZ) for the $3s\ {}^2S$ state in ^{23}Na from equivalent MCDF and MCHF calculations. Shown is also the ratio between the MCDF and MCHF values. In the calculations the active sets for the initial and final states contain the same number of orbitals for each l symmetry, and it is therefore necessary to specify the active set for only one of the states.

Active set	MCDF	MCHF	MCDF / MCHF
DF, HF	635.222	626.645	1.0137
$3s2p1d$	692.287	683.576	1.0127
$4s3p2d1f$	838.286	828.179	1.0122
$5s4p3d2f1g$	871.565	859.807	1.0137
$6s5p4d3f2g1h$	896.576	885.089	1.0130

mated nonrelativistic transition energy of Ref. [32] can be done.

E. Relativistic corrections

All the calculations have been performed in the nonrelativistic LS coupled formalism, and the effect of relativity must be investigated. Qualitatively the relativistic effects manifest themselves in a mass increase

$$m=\frac{m_0}{\sqrt{1-(v/c)^2}}\,, \tag{17}$$

which for inner s- and p-electrons with large average speed leads to a decrease of the effective Bohr radius,

$$a_0=\frac{4\pi\epsilon_0\hbar^2}{me^2}. \tag{18}$$

Due to the different scaling of the hyperfine and transition operators with respect to the radius, the effect of the contraction is to increase the hyperfine interaction constants and decrease the multiplet strength. In this study the relativistic corrections for the hyperfine interaction constants were estimated by multiplying the final nonrelativistic values from the largest calculations by the ratio between Dirac-Fock (DF) and Hartree-Fock (HF) values. To estimate the uncertainty of the relativistic correction factor, a number of fully relativistic multiconfiguration Dirac-Fock (MCDF) calculations were performed for the ${}^2S$ state. The configuration expansions for these calculations were generated by allowing SD excitations from $1s^22s^22p^63s\ {}^2S_{1/2}$ to an increasing active set of orbitals with the restriction that at most single excitations were allowed from the core. In all these calculations the core-orbitals were kept fixed from the DF calculation and only the outer orbitals were varied. Due to stability problems in the relativistic self-consistent field procedure the optimization of the outer orbitals had to be done stepwise so that each time the active set of orbitals was increased only the new orbitals were optimized, whereas all the others were kept fixed. In Table V the MCDF hyperfine interaction constants are compared with equivalent MCHF calculations based on a similar stepwise optimization procedure. Also shown in Table V is the ratio between the MCDF and MCHF values for increasing active sets. This ratio is to a large extent independent of the size of the active set, indicating that the ratio between the DF and HF values is a good measure of the relativistic corrections in the core-valence limit. There is a possibility that core-core and three-particle effects have slightly different relativistic scalings as compared to the core-valence effects. The former effects are, however, comparatively small and so such a difference in scaling will be unimportant. Similar comparisons between MCDF and MCHF values have previously been performed for the ground state of lithium [33]. Also in that case it was found that the ratio between the DF and HF values provides a reliable measure of the relativistic corrections.

For the line strength the relativistic correction was obtained by multiplying the final nonrelativistic value by the ratio between frozen-core DF and HF values. Since the transition program of the MCDF package [34] does not allow the use of nonorthogonal orbitals, a comparison between equivalent MCDF and MCHF values could not be done. To estimate the uncertainty in the relativistic corrections for the line strength we instead performed large MCDF calculations for the resonance transitions in lithiumlike sodium using an orbital set common to both the initial and final state. This simple three electron system allows, even using a common orbital set, for an almost exact treatment, and the final relativistic line strengths were estimated to be correct to within two parts in ten thousand. The ratios between the $1s^22s\ {}^2S_{1/2}-1s^22p\ {}^2P_{1/2}$ and $1s^22s\ {}^2S_{1/2}-1s^22p\ {}^2P_{3/2}$ relativistic line strengths and the corresponding nonrelativistic ones, also correct to within a few parts in ten thousand [35], are 0.9961 and 0.9984, respectively. These very accurate ratios should be compared with the ratios 0.9959 and 0.9981 obtained from frozen-core DF and HF calculations. Assuming that the frozen-core DF and HF corrections behave equally well for neutral sodium, we find that the uncertainty in the final line strength due to the relativistic corrections is only 0.01 a.u. The remaining uncertainties for the line strength are mainly due to the neglected quadruple excitations. We estimate, very conservatively, that the contribution from the latter is less than one-third of the contribution from the triple excitations, that is, less than 0.02 a.u.

IV. COMPARISON WITH EXPERIMENT

In Table VI the final values of the hyperfine interaction constants are compared with the most accurate experimental values and with values obtained with other theoretical methods. As can be seen from the table, the relativistically corrected CI value for the $3s\ {}^2S_{1/2}$ state is very close to the coupled cluster singles and doubles (CCSD) value of Salomonson and Ynnerman [5]. This agreement is very satisfying since both methods, although quite different, include the same important correlation effects. The small difference between the two values can be explained by the four-particle effects included in the CCSD calculation, but neglected in the CI calculation. The values from both these calculations agree to within a few parts in a thousand with the experimental value, showing that the neglected higher-order effects, quintuple-, hexatuple-, etc. are indeed small.

Also for the $3p\ {}^2P_{1/2,3/2}$ states the relativistically corrected CI values for the magnetic dipole interaction constants are in very good agreement with the available experimental

TABLE VI. The interaction constants A_J and B_J for $3s\ {}^2S_{1/2}$ and $3p\ {}^2P_{1/2,3/2}$ states in ^{23}Na compared with values from other calculations and from experiment.

	$3s^2S$	$3p^2P$			
Method	$A_{1/2}$ (MHz)	$A_{1/2}$ (MHz)	$A_{3/2}$ (MHz)	$B_{3/2}/Q$ (MHz/b)	Reference
HF	626.2	63.66	12.72	15.91	This work
CI	870.3	93.16	18.74	25.67	This work
CI [a]	882.2	94.04	18.80	25.79	This work
CCSD [a]	883.8	93.02	18.318	26.14	[5]
RMBPT [b]	860.9	91.40	19.80		[36]
RMBPT [c]	884.5				[37]
FE-MCHF [d]				25.45	[38]
Experiment	885.813 064 4(5)	94.42(19)	18.69(6)		[39–41]
		94.44(13)	18.62(21)		[42]
			18.64(6)		[43]
			18.534(15)		[44]
			18.79(12)		[45]

[a] Corrected for relativistic effects using the ratio between DF and HF values.

[b] Third-order calculation.

[c] All order calculation.

[d] Corrected for relativistic effects using results from quasirelativistic CI calculations.

values. For these states the CCSD calculation did not include any genuine three-particle effects. Comparing the values from the CCSD and CI calculations, it is seen that the greater success of the latter calculation is mainly due to a better description of the three-particle effects.

Since the nuclear quadrupole moment, Q, is inaccurately known from direct nuclear measurements, the theoretical values of the electric quadrupole interaction constant, B, cannot be compared with the experimental values. To enable a comparison between the different theoretical values, the quantity B/Q is reported in Table VI. Whereas there is a very good consistency between the CI and CCSD values for the magnetic dipole interaction constants, this is not the case for B/Q. For this quantity the CCSD value is 1.3% larger than the CI value. Considering the fact that the action of the neglected three-particle effects in the CCSD calculation is to increase the value further, this difference is remarkable.

Accurate values of nuclear quadrupole moments are important for nuclear magnetic resonance relaxation studies. This is particularly true for the biologically relevant sodium. By combining the calculated quantity B/Q with the measured electric quadrupole interaction constant B, a value of the nuclear quadrupole moment can be obtained. Nuclear quadrupole moments can also be obtained from hyperfine splittings of muonic atoms, i.e., atoms where one electron is replaced by a muon. The muonic values have generally been accepted to be fairly accurate, but lately doubts on the accuracy have been cast [38]. Combining the present value of B/Q with the most accurate experimental coupling constant $B=2.724(30)$ MHz [44], a quadrupole moment $Q=105.6$ mb is obtained. This is significantly higher than the muonic value $Q=100.6(20)$ mb. In Table VII quadrupole interaction constants obtained from different methods are compared. As seen from the table, all the values from the atomic or molecular calculations are higher than the muonic value, supporting the conclusion of Ref. [38] that the uncertainty of the muonic values may be larger than expected.

In Table VIII the final value of the multiplet strength in the length form for the $3s\ {}^2S \rightarrow 3p\ {}^2P$ transition is compared with the most accurate experimental values and with values obtained with other theoretical methods. As seen from the table, the relativistically corrected CI value is in good agreement with the value from a previous MCHF calculation that also included some core-core correlation. The difference between these two values is mainly due to the three-particle effects accounted for in the CI calculation, but neglected in the MCHF calculation. The CI value is also in good agreement with the all order RMBPT value of Guet *et al.* [48], the difference being a little more than three parts in a thousand. As in the previous case, a large part of this difference can be

TABLE VII. The nuclear quadrupole moment of ^{23}Na (in mb) from different calculations. The values from the atomic calculations have been obtained by combining B/Q with the experimental quadrupole coupling constant $B=2.724(30)$ MHz of Ref. [44].

Method	$Q({}^{23}\text{Na})$	Reference
hfs + CI calc.	105.6	This work
hfs + FE-MCHF calc.	107.1(2.1)	[38]
hfs + CCSD calc.	104.2	[5]
hfs + molecular calc.	104.2	[46]
Muonic experiment	100.6(20)	[47]

TABLE VIII. The multiplet strength for the $3s\ ^2S \rightarrow 3p\ ^2P$ transition compared with values from other calculations and from experiment.

Method	S	Reference
HF	40.82	This work
CI	37.35	This work
CI [a]	37.26	This work
CCSD [a]	37.56	[5]
RMBPT	37.38	[48]
MCHF-CCP	37.39	[8]
MCHF-CCP [b]	37.30	[8]
Beam laser [c]	37.04(7)	[11]
Beam laser [d]	37.06(9)	[49]
Delayed coincidence [d]	37.04(21)	[41]
Delayed coincidence [c]	37.15(14)	[40]
Beam laser [d]	37.26(5)	[45]
C_3 analysis [d]	37.24(13)	[50]
Linewidth [e]	37.30(9)	[51]

[a] Corrected for relativistic effects using the ratio between DF and HF values.

[b] Value of Ref. [8] corrected for relativistic effects using the ratio between DF and HF values.

[c] Value obtained for the $J=1/2-1/2$ transition.

[d] Weighted value for the $J=1/2-1/2$ and $J=1/2-3/2$ transitions.

[e] Value obtained for the $J=1/2-3/2$ transition.

explained by a different description of the three-particle effects.

Upon a comparison with the experimental values, it is seen that the relativistically corrected CI value is in very good agreement with the values from a number of new measurements [45,50,51]. Thus, the previous disagreement between the theoretical and experimental values at the percent level is now resolved.

V. SUMMARY AND CONCLUSIONS

We report large-scale MCHF and CI calculations of the transition probability and hyperfine structures in the sodium $3s\ ^2S-3p\ ^2P$ resonance transition. In the calculations the orbital sets of the initial and final state wave functions were not assumed to be the same, but were optimized independently. The evaluation of the transition matrix elements was done using a technique where the two orbital sets are transformed to become biorthonormal, in which case standard Racah algebra can be used. The configuration expansion was generated with the active space method, where CSF's of a particular parity and LS symmetry are generated by excitations from one or more reference configurations to an active set of orbitals. The active set was increased in a systematic way, allowing for the convergence of the multiplet strength and the hyperfine structure constants to be studied. In the calculations the first correlation orbitals were targeted to describe core-valence effects and not until these effects were saturated were core-core effects included. The effect on the hyperfine structure and multiplet strength from the CSF's describing core-core correlation was found to be mainly indirect, through the action on the expansion coefficients of the CSF's describing core-valence effects. Three-particle effects were included in the CI calculations and were found to be of importance for the hyperfine interaction but unimportant for the multiplet strength. The calculated hyperfine interaction constants for the $3s\ ^2S_{1/2}$ and $3p\ ^2P_{1/2,3/2}$ states all agree to within less than 0.7% with the experimental values. The calculated multiplet strength is in perfect agreement with the most recent experimental values resolving the long-standing disrepancy between theory and experiment for this transition.

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[1] S.A. Blundell, W.R. Johnson, Z.W. Liu, and J. Sapirstein, Phys. Rev. A **40**, 2233 (1989).

[2] F.W. King, Phys. Rev. A **40**, 1735 (1989).

[3] A.-M. Mårtensson-Pendrill and A. Ynnerman, Phys. Scr. **41**, 329 (1989).

[4] D. Sundholm and J. Olsen, Phys. Rev. A **42**, 2614 (1990).

[5] S. Salomonson and A. Ynnerman, Phys. Rev. A **43**, 88 (1991).

[6] P. Jönsson, Phys. Scr. **48**, 678 (1993).

[7] J. Carlsson, P. Jönsson, M.R. Godefroid, and C. Froese Fischer, J. Phys. B **28**, 3729 (1995).

[8] T. Brage, C. Froese Fischer, and P. Jönsson, Phys. Rev. A **49**, 2181 (1994).

[9] R.N. Barnett, E.M. Johnson, and W.A. Lester, Jr., Phys. Rev. A **51**, 2049 (1995).

[10] U. Volz (private communication).

[11] A. Gaupp, P. Kuske, and H.J. Andrä, Phys. Rev. A **26**, 3351 (1982).

[12] W.I. McAlexander, E.R.I. Abraham, N.W.M. Ritchie, C.J. Williams, H.T.C. Stoof, and R.G. Hulet, Phys. Rev. A **51**, R871 (1995).

[13] W.D. Robb, Comput. Phys. Commun. **6**, 132 (1973).

[14] C. Froese Fischer, M.R. Godefroid, and A. Hibbert, Comput. Phys. Commun. **64** 486 (1991).

[15] P.Å Malmqvist, Int. J. Quantum Chem. **30**, 479 (1986).

[16] J. Olsen, M.R. Godefroid, P. Jönsson, P.Å Malmqvist, and C. Froese Fischer, Phys. Rev. E **52**, 4499 (1995).

[17] L. Sturesson and C. Froese Fischer, Comput. Phys. Commun. **74**, 432 (1993).

[18] A. Hibbert and C. Froese Fischer, Comput. Phys. Commun. **64**, 417 (1991).

[19] C. Froese Fischer, Comput. Phys. Commun. **64**, 431 (1991).

[20] P. Jönsson, C.-G. Wahlström, and C. Froese Fischer, Comput. Phys. Commun. **74**, 399 (1993).

[21] C. Froese Fischer and M.R. Godefroid, Comput. Phys. Commun. **64**, 501 (1991).

[22] A. Stathopoulos, A. Ynnerman, and C. Froese Fischer, Int. J. Supercomp. Appl. High Perf. Comput. **10**, 41 (1996).

[23] C. Froese Fischer, Comput. Phys. Commun. **64**, 369 (1991).

[24] E.R. Davidson, J. Comput. Phys. **17**, 87 (1975).

[25] A. Stathopoulos and C. Froese Fischer, Comput. Phys. Commun. **64**, 268 (1994).

[26] P. Raghavan, At. Data Nucl. Data Tables **42**, 189 (1989).

[27] R.D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981), Chap. 14.

[28] J. Carlsson, P. Jönsson, L. Sturesson, and C. Froese Fischer (unpublished).

[29] B.O. Roos, P.R. Taylor, and P.E.M. Siegbahn, Chem. Phys. Lett. **48**, 157 (1980).

[30] J. Olsen, B.O. Roos, P. Jørgensen, and H. J. A. Jensen, J. Chem. Phys. **89**, 2185 (1988).

[31] B. Engels, Theor. Chim. Acta **86**, 429 (1993).

[32] C. Froese Fischer, Nucl. Instrum. Methods B **31**, 265 (1988).

[33] J. Carlsson, P. Jönsson, and C. Froese Fischer, Phys. Rev. A **46**, 2420 (1992).

[34] F.A. Parpia, C. Froese Fischer, and I.P. Grant, Comput. Phys. Commun., (to be published).

[35] M. Godefroid, C. Froese Fischer, and P. Jönsson, Phys. Scr., (to be published).

[36] W.R. Johnson, M. Idrees, and J. Sapirstein, Phys. Rev. A **35**, 3218 (1987).

[37] Z. Liu, Ph.D. thesis, University of Notre Dame (1989).

[38] D. Sundholm and J. Olsen, Phys. Rev. Lett. **68**, 927 (1992).

[39] A. Beckman, K. D. Böklen, and D. Elke, Z. Phys. **270**, 173 (1974).

[40] J. Carlsson, P. Jönsson, L. Sturesson, and C. Froese Fischer, Phys. Scr. **46**, 394 (1992).

[41] J. Carlsson, Z. Phys. D **9**, 147 (1988).

[42] W.A. Wijngaarden and J. Li, Z. Phys. D **32**, 67 (1994).

[43] Th. Krist, P. Kuske, A. Gaupp, W. Wittmann, and H.J. Andrä, Phys. Lett. **A61**, 94 (1977).

[44] W. Yei, A. Sieradzan and M.D. Havey, Phys. Rev. A **48**, 1909 (1993).

[45] U. Volz, M. Majerus, H. Liebel, A. Schmitt, and H. Schmoranzer, Phys. Rev. Lett. **76**, 2862 (1996).

[46] P. Pyykkö and A.J. Sadlej, Chem. Phys. Lett. **227**, 221 (1994).

[47] B. Jeckelmann, W. Beer, I. Beltrami, F.W.N. de Boer, G. de Chambrier, P.F.A. Goudsmit, J. Kern, H.J. Leisi, W. Ruckstuhl, and A. Vacchi, Nucl. Phys. A **408**, 495 (1983).

[48] C. Guet, S.A. Blundell, and W.R. Johnson, Phys. Lett. A **143**, 384 (1990).

[49] H. Schmoranzer, D. Schulze-Hagenest, and S.A. Kandela (unpublished).

[50] H. Richling, H. Knöckel, and E. Tiemann (private communication).

[51] C. Oates, K. Vogel, and J. L. Hall, Phys. Rev. Lett. **76**, 2866 (1996).