

## Failure of multiconfiguration Dirac-Fock wave functions in the nonrelativistic limit

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Multiconfiguration Dirac-Fock (MCDF) wave functions for a specific  $J$  quantum number may not reduce to the appropriate nonrelativistic limit for the  $L$  and  $S$  quantum numbers. Transition probabilities calculated from such MCDF wave functions for spin-forbidden transitions are unreliable. Remedies for this problem are discussed, including the advantages of using nonorthogonal radial orbitals. It is also shown that transition probabilities for weak transitions are sensitive to the way the Breit interaction is introduced.

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We show that in the nonrelativistic (NR) limit some multiconfiguration Dirac-Fock (MCDF) wave functions for atoms may not reflect the correct total orbital angular momentum  $L$  and total spin  $S$ , and consequently lead to seriously erroneous transition probabilities for weak transitions, such as spin-forbidden ones. We also demonstrate that the Breit interaction affects MCDF wave functions sufficiently so as to alter transition probabilities for weak transitions by 20–30 %.

In the MCDF method, a relativistic total wave function is constructed in analogy to the NR multiconfiguration Hartree-Fock (MCHF) method. The MCDF method uses relativistic four-component one-electron orbitals  $\psi_{n\kappa m}$ —with principal quantum number  $n$ , Dirac quantum number  $\kappa$ , and  $m$  the projection of the angular momentum  $j$ —to build a configuration state function (CSF)  $\Phi_{JM}$  using  $jj$  coupling to be an eigenfunction of the total angular momentum  $J$ , its projection  $M$ , and parity. Then, a MCDF wave function  $\Psi_{JM}$  is constructed as a linear combination of the CSF's. The coefficients of this linear combination are known as the configuration mixing coefficients.

As is commonly done in the MCHF method, the configuration mixing coefficients and radial functions are determined in the MCDF method by applying the self-consistent field (SCF) procedure to both of them. The level of electron correlation represented by a MCDF wave function is determined by the type and number of CSF's included in  $\Psi_{JM}$ .

For example, the most significant part of the electron correlation in the  $2s2p$ ,  $J=1$  level of Be can be represented by introducing one additional NR configuration  $2p3d$  (the  $K$  shell is omitted for simplicity):

$$\begin{aligned} \Psi_{J=1} = & a\Phi(2s_{1/2}2p_{1/2}) + b\Phi(2s_{1/2}2p_{3/2}) \\ & + c\Phi(2p_{1/2}3d_{3/2}) + d\Phi(2p_{3/2}3d_{3/2}) \\ & + e\Phi(2p_{3/2}3d_{5/2}). \end{aligned} \quad (1)$$

The MCDF method produces more compact wave functions to account for the electron correlation than other methods in which radial functions are kept frozen and only the mixing coefficients are subjected to the SCF process, since CSF's with singly excited configurations need not be included in the MCDF method.

We found an unexpected source of error in the transition probabilities calculated from MCDF wave functions. This error occurs only when both radial functions and configuration mixing coefficients are determined through the SCF procedure, and hence this is a problem peculiar to relativistic formulations with fully relaxed radial functions, such as in the MCDF method.

A MCDF wave function is required to be an eigenfunction of  $J$ , but not  $L$  and  $S$  separately. For a MCDF wave function to be a simultaneous eigenfunction of  $L$ ,  $S$ , and  $J$  in the NR limit, the relativistic one-electron orbitals with the same orbital angular momentum  $l$  but different  $j$  must have a certain ratio in this limit. If this ratio is different in two or more configurations used in a MCDF wave function, then this wave function will not have definite values of  $L$  and  $S$  in the NR limit. Computationally, the NR limit of a relativistic wave function is attained by letting the speed of light increase to infinity—actually  $c \geq 10^4$  in atomic units (the actual value of  $c$  is 137.036 in a.u.) is sufficient.

The Schrödinger equation is correct in the NR limit; one can easily show that the Dirac-Fock equation for a many-

TABLE I.  $A_{ki}$  ( $s^{-1}$ ) for the  $2s2p\ ^3P_1 \rightarrow 2s^2\ ^1S_0$  transition of  $B^+$  and  $C^{2+}$ .

Source	$A_{ki}(B^+)$	$A_{ki}(C^{2+})$
Weiss, large scale MCHF [8]		106.7
Froese Fischer and Gaigalas, large scale MCHF [9]	$10.27 \pm 0.20$	$103.0 \pm 0.4$
Present work, MCDF		
Orthogonal orbitals, without the Breit interaction		
$2s2p+2p3d$ without the NR offset subtracted	341.3	301.7
with the NR offset subtracted	11.43	113.2
Orthogonal orbitals, with the Breit interaction		
$2s2p+2p3d$ without the NR offset subtracted	317.2	248.2
with the NR offset subtracted	7.38	81.4
Nonorthogonal orbitals		
$2s2p+2p'3d$ without the Breit interaction	11.46	113.7
with the Breit interaction	7.37	81.8
$n \leq 4$ + Breit+core excited configurations	9.01	94.4
$n \leq 5$ + Breit+core excited configurations	9.13	100.1
Jönsson and Froese Fischer, relativistic, $n \leq 8$ [10]		$102.9 \pm 1.5$
Doerfert <i>et al.</i> , experiment [11]		$102.9 \pm 0.14$

electron atom reduces correctly to the matching Hartree-Fock equation in the  $c \rightarrow \infty$  limit [1]. Hence, one must select among the solutions of the MCDF equation those that have the correct NR limit. For the last 30 years during which many researchers have used the MCDF method, it was *assumed* that MCDF wave functions would reduce to the correct NR limit, without verification of the limiting values of  $L$  and  $S$  in each case. We found that *the calculated MCDF wave functions sometimes fail to reduce to the eigenfunctions of  $L$  and  $S$ , when the ratios of the one-electron orbitals with  $j=l-1/2$  and  $j=l+1/2$  in all configurations are not the same.*

An example of this difficulty is seen in the MCDF wave function shown in Eq. (1). For the  $^3P_1$  level, the square of the ratio of the  $2p_{1/2}$  and  $2p_{3/2}$  orbitals in the first two relativistic configurations is 2:1 in the  $LS$  limit; while the square of the ratio in the last three relativistic configurations is 1:5. In contrast, the squares of the same ratios for the  $^1P_1$  level are 1:2 in both sets of configurations [2].

Thus a MCDF wave function with the configurations indicated in Eq. (1) will have an incorrect NR limit for the  $^3P_1$  level (the lowest  $J=1$ ), while it will have the correct limit for the  $^1P_1$  level (the second lowest  $J=1$  level). This implies that the MCDF wave function for the lowest  $J=1$  level will be a mixture of different  $LS$  states in the NR limit. Among the  $LS$  states that can be formed by the  $2s2p$  and  $2p3d$  configurations, we found that the MCDF wave function for the lowest  $J=1$  level contains a trace of the  $^1P_1$  level in the NR limit.

The  $^1P_1 \rightarrow ^1S_0$  transition is dipole allowed and its probability (expressed in terms of the Einstein  $A_{ki}$  coefficient between an upper level  $k$  and a lower level  $i$ ) is very large even in the NR limit, while the  $^3P_1 \rightarrow ^1S_0$  transition is spin forbidden and should vanish in the NR limit. A small admixture of the singlet configuration in the triplet wave function introduces a nonvanishing contribution in the NR limit, which remains as a residue in the transition matrix element. We call this ‘‘residue’’ a NR offset, and we can determine its magnitude easily from the transition matrix element between

appropriate MCDF wave functions calculated in the  $c \rightarrow \infty$  limit.

To get the correct magnitude of the transition matrix element, this NR offset must be subtracted from the same transition matrix element calculated with the correct value of  $c$ . In Table I we compare  $A_{ki}$  for the  $2s2p\ ^3P_1 \rightarrow 2s^2\ ^1S_0$  transition in Be-like ions  $B^+$  and  $C^{2+}$  to demonstrate, *inter alia*, the effect of the NR offset when MCDF wave functions are used.

The rows marked ‘‘ $2s2p+2p3d$ ’’ used MCDF wave function in Eq. (1) for the  $2s2p\ ^3P_1$  level and

$$\Psi_{J=0} = a' \Phi(2s_{1/2}^2) + b' \Phi(2p_{1/2}^2) + c' \Phi(2p_{3/2}^2) + d' \Phi(3d_{3/2}^2) + e' \Phi(3d_{5/2}^2) \quad (2)$$

for the ground state,  $2s^2\ ^1S_0$ .

The NR offset in the  $^3P_1 \rightarrow ^1S_0$  transition of Be-like  $B^+$  affects the  $A_{ki}$  value by a factor of 30. Results for  $C^{2+}$  are also compared in Table I. Similar large NR offsets in the  $A_{ki}$  values for this transition from MCDF wave functions can be found in Ref. [3].

Another example of a NR offset resulting from incorrect NR limits of MCDF wave functions is found in the calculated fine-structure splitting of some open-shell atoms [4]. Errors in such a case can also be corrected by subtracting appropriate NR offsets.

The magnitude of this NR offset depends on the number and type of extra configurations used in a MCDF wave function. It turns out that the occurrence of a nonvanishing NR offset in the transition matrix element is the rule rather than an exception when MCDF wave functions with many configurations are used. The  $^1P_1$  level (the second lowest  $J=1$ ) from the MCDF wave function in Eq. (1) is an exception because the ratios of the  $2p_{1/2}$  and  $2p_{3/2}$  orbitals for the  $^1P_1$  limit are the same in the  $2s2p$  and the  $2p3d$  configurations.

Subtraction of NR offsets from MCDF transition matrix elements is a straightforward way to correct for the unpre-

dictable errors introduced when MCDF wave functions do not converge to the correct NR limit.

Another obvious remedy is to give up on the MCDF method and rely solely on a large set of frozen radial functions. For instance, one can generate an initial set of “configuration average” radial functions that correspond to the  $2J+1$  weighted average of all possible  $J$ 's that can be constructed from the configurations included in a calculation. This choice, however, usually requires very many configurations to achieve high accuracy in representing electron correlation.

A third option for remedy is the use of nonorthogonal radial functions. For instance, if we use  $2p$  in the  $2s2p$  configurations and  $2p'$  in the  $2p'3d$  configurations in Eq. (1), then the relativistic  $2p$  and  $2p'$  radial functions, which are not orthogonal to each other, can maintain separate ratios for  $j = 1/2$  and  $3/2$ , and converge to the common, correct NR limits of  $L$  and  $S$ . The NR offset results from the requirement that the one-electron orbitals with the same quantum numbers be identical in all configurations in a MCDF wave function. Once we remove this requirement, NR offsets vanish. The row marked “ $2s2p+2p'3d$ ” in Table I contains such results, and they are in excellent agreement with the results with orthogonal orbitals from which the NR offsets have been subtracted.

Nonorthogonal orbitals offer more flexibility than orthogonal orbitals, and the former represent electron correlation better. For instance, it is easy to introduce core-valence correlation using two nonorthogonal orbitals, one for correlating to core orbitals, and the other to account for the valence shell correlation. The former will have the radial size of the core orbitals, while the latter will have the size of the valence shell.

The row marked “ $n \leq 5 + \text{core excited configurations}$ ” in Table I contains results from MCDF wave functions that included nonorthogonal orbitals with  $n \leq 5$  and single and double excitations of the  $1s$  electrons to  $2p$ . These MCDF wave functions include the relativistic equivalent of less than a dozen NR configurations, clearly demonstrating the high efficiency of nonorthogonal radial functions in representing electron correlation. To generalize the use of nonorthogonal radial functions, however, we must modify much of the atomic-structure theory, and keep overlap integrals between nonorthogonal radial functions in all expressions for atomic properties, such as the total energy and transition probabilities.

In summary, for strong transitions, the NR offset is many orders of magnitude smaller than the transition matrix element, and hence its omission does not cause any noticeable error. For weak transitions, however, NR limits of MCDF wave functions must be examined carefully lest the results be spoiled by erroneous and unpredictable NR offsets. For any

transition that is forbidden in the NR limit, one can check for the existence of a nonvanishing NR offset by simply calculating the  $A_{ki}$  value while setting  $c \rightarrow \infty$ . If a nonvanishing NR offset exists, then that value must be subtracted from the transition matrix element calculated using the correct value of  $c$ .

In the MCDF method, it is common to include only the Dirac one-electron Hamiltonian and the Coulomb repulsion,  $e^2/r_{ik}$ , between the  $i$ th and  $k$ th bound electrons in the SCF process [5,6]. Then, the Breit interaction, which is the relativistic correction to the Coulomb repulsion, is calculated in the first order perturbation. In this way, only the total energy but not the wave function is affected by the Breit interaction.

In our version of the MCDF code [5,7], we have the option to include the magnetic interaction part of the Breit interaction in the SCF process and rediagonalize the Hamiltonian matrix after including other contributions from the Breit interaction. Another option is not to include any part of the Breit interaction in the SCF process, but include them all in the Hamiltonian matrix after the SCF process and diagonalize the matrix. The former procedure will modify both one-electron radial functions and the configuration mixing coefficients through the Breit interaction, while the latter procedure will change only the configuration mixing coefficients. Although these two alternatives lead to almost the same result for light atoms as expected, the former procedure will lead to a better result for heavy atoms, where relativistic effects are significant. The results marked “with the Breit interaction” in Table I clearly demonstrate the importance of incorporating changes in the wave function due to the Breit interaction before transition probabilities are calculated. *This requirement applies to all types of wave functions, not just MCDF wave functions.*

Finally the results in Table I also indicate the importance of including a large number of configurations to account fully for electron correlation, which still remains as the most difficult and challenging aspect of atomic-structure theory.

The use of nonorthogonal one-electron radial functions is not only a proven way to avoid nonvanishing NR offsets, but is also a promising way to account for the core-valence correlation, which has been difficult to achieve with an orthogonal set of one-electron radial functions. A more systematic study of nonorthogonal radial functions is desirable to explore their full potential.

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