Comment on relativistic transition-probability calculations for the Be isoelectronic sequence*

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Recent calculations of oscillator strengths by Armstrong, Fielder, and Lin employing relativistic multiconfiguration Hartree-Fock (MCHF) methods give a disparity between length- and velocity-gauge results. It is shown here that the disparity is due in part to the neglect of certain "exchange overlap" terms in the evaluations of transition-matrix elements in MCHF calculations. Including such exchange overlap terms brings velocity-gauge values into substantial agreement with length-gauge results for high-Z members of the Be isoelectronic sequence. The disparity for lower members of the sequence is increased and the resulting difference between length- and velocity-gauge values reflects the changing reliability of the MCHF calculation as Z increases along the sequence.

Interest in calculations of excitation energies and oscillator strengths for highly charged ions has increased in the last few years because of the importance of such ions for plasma diagnostics,[1] in astrophysics,[2] and in laboratory beam-foil measurement.[3] Progress has been made recently by Kim and Desclaux[4] and by Armstrong, Fielder, and Lin[5] in evaluating some of the required atomic data using relativistic multiconfiguration Hartree-Fock (MCHF) methods.

A problem encountered in approximate calculations such as those of Refs. 4 and 5 is that transition rates depend on the gauge of the radiation field; different gauges lead to different rates. As pointed out by Grant,[6] one particular gauge (we call it the length gauge) leads to length-form oscillator strengths, f_L; while another gauge (the velocity-gauge, or the Coulomb-gauge) leads to velocity-form oscillator strengths, f_V.

An immediate question arises as to which gauge is best to use in a particular calculation. Recent studies by Starace[7] indicate that the length gauge is to be preferred in MCHF calculations. In fact, theoretical calculations of f_V are especially sensitive to the small distance features of atomic structure,[8] so that particular care is required usually when evaluating f_V. In any case, determinations of both f_L and f_V are of interest since gauge invariance is a fundamental physical constraint, and differences between f_L and f_V provide a guide to the reliability of approximate calculations. Further discussion on the difference between f_L and f_V and on their connections with the present work is given in Appendix A.

As a case in point, let us consider the calculations of the resonance transition $^1S_0$-$^1P_1$ along the Be isoelectronic sequence given by Armstrong, Fielder, and Lin in Ref. 5. In the calculation of Ref. 5, the initial excited state was a $J=1$ superposition of the two configurations $(2s_{1/2}2p_{1/2})$ and $(2s_{1/2}2p_{3/2})$. The final $J=0$ state was a combination of the $(2s_{1/2})^2$, $(2p_{1/2})^2$, and $(2p_{3/2})^2$ configurations. The frequency-dependent electric dipole transition operators in the length and velocity gauges were used to determine f_L and f_V. Transition frequencies included contributions from the Breit interaction whereas atomic orbitals were determined without the Breit correction. Both f_L and f_V were determined along the sequence from B^{+1} to U^{+88}; these results are reproduced in columns 2 and 3 of Table I. One sees that discrepancies between f_L and f_V are fairly small along the entire sequence. One rather surprising feature of the comparison is that the discrepancies remain more or less constant along the sequence, contrary to the expectation that f_L and f_V should agree better and better with increasing Z because of the diminishing role of correlations. It is our purpose here to show that part of the discrepancy, in particular that occurring at high Z, is mainly due to an approximation made in evaluating the MCHF transition matrix elements, and is not inherent in the MCHF method.

When evaluating matrix elements of the transition operator in MCHF calculations, account must be taken of the fact that initial-state orbitals and final-state orbitals belong to different orthonormal sets of functions. The transition matrix elements consists of a sum of "direct overlap" terms which connect identical single-particle orbitals in the initial and the final states, and "exchange overlap" terms which come from nonzero overlaps of orbitals from different subshells. A detailed discussion of these terms in the Be case is given in Appendix B. In calculations such as those of Refs. 4 and 5, the exchange overlap terms are neglected. In the present calculation, by contrast, both direct and exchange overlap terms are retained.

The results of the present calculation for the resonance transition are presented in columns

TABLE I. Relativistic oscillator strengths (length and velocity) for Be-isoelectronic sequence.

Elements	$^1S_0$-$^1P_1$				$^1S_0$-$^3P_1$			
	f_L[a]	f_V[a]	f_L[b]	f_V[b]	f_L[a]	f_V[a]	f_L[b,c]	f_V[b,c]
B^{+1}	1.069	0.867	1.067	0.799	$<10^{-8}$	$<10^{-8}$	1.9×10^{-8}	9.6×10^{-9}
C^{+2}	0.791	0.680	0.788	0.595	$<10^{-7}$	$<10^{-7}$	1.2×10^{-7}	6.9×10^{-8}
N^{+3}	0.631	0.573	0.628	0.482	$<10^{-7}$	$<10^{-7}$	4.3×10^{-7}	2.8×10^{-7}
O^{+4}	0.527	0.499	0.524	0.407	$<10^{-6}$	$<10^{-6}$	1.2×10^{-6}	8.4×10^{-7}
F^{+5}	0.452	0.444	0.450	0.353	$<10^{-6}$	$<10^{-6}$	2.8×10^{-6}	2.1×10^{-6}
Ne^{+6}	0.397	0.401	0.395	0.313	$<10^{-6}$	$<10^{-6}$	5.8×10^{-6}	4.4×10^{-6}
Ar^{+14}	0.209	0.240	0.208	0.173	2.2×10^{-4}	3.0×10^{-4}	2.2×10^{-4}	1.9×10^{-4}
Fe^{+22}	0.156	0.190	0.155	0.136	0.0015	0.0024	0.0015	0.0015
Kr^{+32}	0.137	0.171	0.137	0.128	0.0054	0.0089	0.0053	0.0052
Mo^{+38}	0.140	0.172	0.140	0.134	0.0075	0.0127	0.0075	0.0073
Xe^{+50}	0.168	0.193	0.168	0.166	0.0096	0.0158	0.0096	0.0092
Gd^{+60}	0.209	0.231	0.210	0.209	0.0099	0.0157	0.0099	0.0093
W^{+70}	0.265	0.284	0.267	0.266	0.0099	0.0150	0.0099	0.0090
Pb^{+78}	0.320	0.339	0.323	0.322	0.0098	0.0143	0.0098	0.0087
U^{+88}	0.403	0.421	0.409	0.406	0.0097	0.0136	0.0097	0.0084

[a]Reference 5.
[b]This calculation.
[c]See footnote 10.

4 and 5 of Table I. Comparing the present calculation with that of Ref. 5, we see that the length-gauge values are changed only slightly by the inclusion of exchange overlap terms. This observation is in harmony with the conclusions of Ref. 7, and illustrates the appropriateness of the length gauge in MCHF calculations. Velocity-gauge values are found to be significantly modified by the exchange overlap terms. Comparing the present values of f_L and f_V, we find that much of the discrepancy at high Z in the older calculation has been removed, while the difference between f_L and f_V at low Z is increased. The poor agreement between f_L and f_V at small Z is a reflection of the small number of configurations used in the MCHF calculations; by increasing the number of configurations, it has been shown that the discrepancy between f_L and f_V can be substantially improved.[9] The good agreement at high Z is expected because of the dominant role of the central nuclear field.

It is worthwhile mentioning here that at high Z, there is a small residual difference between f_L and f_V even in the present calculation. This residue results partly from the approximate nature of the MCHF calculation and partly from the very rough treatment of the Breit interaction in the present relativistic calculation.

In columns 6 and 7 of Table I, we list values of f_L and f_V for the intercombination transition $^1S_0$-$^3P_1$ from Armstrong, Fielder, and Lin.[5] Our comparison values of f_L and f_V, given in columns 8 and 9, agree better than the corresponding values of the older calculation throughout the entire sequence.[10] Again, it should be noticed that the length gauge results are not substantially modified by exchange overlap terms, only the velocity-gauge results are changed appreciably.

Inspection of columns 8 and 9 shows that the discrepancy between f_L and f_V increases in the present calculation in the range $Z = 54$–92. We believe that this increase is a result of the present approximate treatment of the Breit interaction (neglecting Breit orbital corrections and using configuration averaged Breit energies). The forbidden transition rate is sensitive to relativistic effects so that a more careful treatment of the Breit interaction than used in this approximate calculation is required to reduce the residual difference beyond that given here.

It has been our purpose above to illustrate the sensitivity of velocity-form oscillator strengths f_V to exchange overlap terms which occur in MCHF calculations. By including such terms in relativistic MCHF calculations, we are able to bring values of f_V into close agreement with corresponding values of f_L. The small residual difference between f_L and f_V at high Z in the present calculation is due partly to the approximate MCHF calculations and partly to the rough treatment of the Breit interaction; while the disagreement at low Z is due primarily to the small number of configurations used in the present calculation.

APPENDIX A

In the above discussions, we have pointed out that the exchange overlap terms are responsible for part of the difference between f_L and f_V reported in the literature. Below we discuss in more

detail the origin of this difference and our approach to the calculation.

As pointed out by Grant,[6] the discrepancy between f_L and f_V in a relativistic theory is due to the different choices of gauge in which the electromagnetic potentials are written. In general, for electric multipole transitions, the "length-form" transition operator M_L and the "velocity-form" transition operator M_V are related through the gauge transformation:

$$M_L = M_V + \Delta M. \tag{A1}$$

Where ΔM is also a transition operator given explicitly in Ref. 6. Let $|i\rangle$ and $|f\rangle$ be the initial and the final states, respectively; then from Eq. (A1), we have

$$\langle f|M_L|i\rangle = \langle f|M_V|i\rangle + \langle f|\Delta M|i\rangle. \tag{A2}$$

Gauge invariance requires that the gauge term $\langle f|\Delta M|i\rangle$ should be zero. This is, however, not true in Hartree-Fock or MCHF calculations because of the approximate treatment of the correlation effects. As a result, the gauge term is responsible for the "intrinsic" difference between f_L and f_V.

Complications can arise, however, in actual calculations. Errors from numerical inaccuracy or from specific approximations employed (e.g., neglecting the exchange overlap terms) in the evaluation of the transition matrix elements must be considered along with the gauge terms to give an "apparent" difference between f_L and f_V. At this point, it becomes clear that the inclusion of the exchange overlap terms just represents the correct way to evaluate transition matrix elements, and that by including these terms, we do not expect to reduce the "intrinsic" difference between f_L and f_V but rather to bring out the actual discrepancy present in the MCHF calculations.

APPENDIX B

When the single-particle wave functions making up the initial and final states are not identical, there will be nonzero overlap matrix elements between orbitals from different subshells having the same angular symmetries. For such wave functions, the transition matrix elements will consist of a sum of two types of terms: (1) "direct-overlap" terms connecting identical single-particle orbitals in the initial and final states, and (2) "exchange-overlap" terms arising from the nonzero overlaps of orbitals from different subshells. These exchange overlap terms would otherwise be forbidden by the orthornormality of single-particle wave functions. Detailed evaluations of transition matrix elements using nonorthogonal basis sets are given by Löwdin.[11]

As an example, consider the transition rate calculations for Be-like ions. In our present case, the initial- and final-state wave functions are given by

$$\psi_{J=1} = d_1\psi_1(2s\,2\bar{p}) + d_2\psi_1(2s\,2p),$$

$$\psi_{J=0} = c_1\psi_0(2s^2) + c_2\psi_0(2\bar{p}^2) + c_3\psi_0(2p^2).$$

Here, for simplicity, we have denoted $2p_{1/2}$ by $2\bar{p}$ and $2p_{3/2}$ by $2p$. The coefficients c_i and d_i are configuration weighting factors, and $\psi_J(a,b)$ are antisymmetric wave functions constructed from Slater determinant wave functions $\psi(j_a m_a, j_b m_b)$:

$$\psi_J(a,b) = \sum_{m_a m_b} c(j_a j_b J; m_a m_b m)\,\psi(j_a m_a, j_b m_b).$$

Let M be any one-particle transition operator; direct calculation shows

$$\begin{aligned}\langle\psi_{J=0}|M|\psi_{J=1}\rangle = {} & c_1d_1[\langle 1s|1s\rangle\langle 2s|2s\rangle - \langle 1s|2s\rangle\langle 2s|1s\rangle][\langle 1s|1s\rangle\langle 2s|M|2\bar{p}\rangle - \langle 2s|1s\rangle\langle 1s|M|2\bar{p}\rangle] \\ & + c_1d_2[\langle 1s|1s\rangle\langle 2s|2s\rangle - \langle 1s|2s\rangle\langle 2s|1s\rangle][\langle 1s|1s\rangle\langle 2s|M|2p\rangle - \langle 2s|1s\rangle\langle 1s|M|2p\rangle] \\ & + c_2d_1\langle 1s|1s\rangle\langle 2\bar{p}|2\bar{p}\rangle[\langle 1s|1s\rangle\langle 2\bar{p}|M|2s\rangle - \langle 1s|2s\rangle\langle 2\bar{p}|M|1s\rangle] \\ & + c_3d_2\langle 1s|1s\rangle\langle 2p|2p\rangle[\langle 1s|1s\rangle\langle 2p|M|2s\rangle - \langle 1s|2s\rangle\langle 2p|M|1s\rangle].\end{aligned}$$

In the above relation, $\langle a|b\rangle$ denotes the overlap matrix element between orbitals a and b in the final and the initial states, respectively. For simplicity, the Clebsch-Gordan coefficients are absorbed in the one-particle transition matrix elements, $\langle a|M|b\rangle$. For this case, the direct overlap terms are obviously given by

$$\begin{aligned}& c_1d_1\langle 1s|1s\rangle^2\langle 2s|2s\rangle\langle 2s|M|2\bar{p}\rangle + c_1d_2\langle 1s|1s\rangle^2\langle 2s|2s\rangle\langle 2s|M|2p\rangle + c_2d_1\langle 1s|1s\rangle^2\langle 2\bar{p}|2\bar{p}\rangle\langle 2\bar{p}|M|2s\rangle \\ & \quad + c_3d_2\langle 1s|1s\rangle^2\langle 2p|2p\rangle\langle 2p|M|2s\rangle,\end{aligned}$$

while the remaining terms are the exchange overlap terms which involve all the nonzero overlap matrix elements $\langle a|b\rangle$ with $a \neq b$. It is just these exchange overlap terms which are ordinarily omitted in MCHF calculations but which are included here.

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