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Crucial Role of Electron Correlation in Both the Upper and Lower States in Optical Transitions

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It is demonstrated that the specifically non-closed shell type correlation effects of the Non-Closed Shell Many-Electron (NCMET) Electronic Structure theory of Sinanoğlu, in both states of an allowed transition affect the electric dipole oscillator strengths by large factors. Detailed Hartree-Fock and NCMET calculations on the Cl III $3s^2 3p^3 (^4S^\circ) \rightarrow 3s3p^4 (^4P)$ display the effect.

Key words: Oscillator strength – Electron correlation – Optical transitions – Non-closed shell theory

Allowed electric dipole transition probabilities (A_{if}) and the closely related oscillator strengths (f_{E1}) are of theoretical interest being very sensitive to details of electron correlation in both ground and excited states, thus providing a stringent test of many electron theories. This is particularly true for "in-shell" transitions such as $1s^2 2s^2 2p^2 \rightarrow 1s^2 2s 2p^3 (KL \rightarrow KL')$ which involve rearrangement of all the valence shell electrons during the transition and thus reflect the correlation effects significantly.

Atomic transitions are of crucial importance in determination of chemical abundances and stellar evolution models in astrophysics and in other applications in atmospheric and solar physics, and have been tabulated by the U.S. National Bureau of Standards [1].

Such transitions were previously measured by emission or absorption techniques in arcs and furnaces. These "intensity" methods require an independent determination of the atom density in the initial state. That determination has turned out difficult and the equilibrium assumptions usually made have turned out incorrect thus leading to errors of the order of a factor of 2–3 for atoms like C, N, O, and factors like 10–30 for heavier atoms like Si, S, Cl, and Fe. The NBS tables [1] summarize data from the literature from diverse experimental and theoretical sources. Until very recently, the theoretical values used were based on

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This article is dedicated to Professor H. Hartmann and to his efforts which have been so important in the development of theoretical chemistry in post-war Germany.

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the Hartree-Fock (RHF) method, sometimes with a small amount of configuration interaction, and at times on a Z-dependent perturbation theory. These values too, as shown recently in papers by Sinanoğlu [2] and Westhaus and Sinanoğlu [3] have turned out to be in error, frequently by factors similar to those in the intensity measurements.

Single configuration methods, such as RHF and particular applications of the Z-dependent perturbation theory, in the absence of internal correlation, such as $ns^2 \leftrightarrow np^2$, become quite good at higher Z's along an isoelectronic sequence where non-internal type correlation effects become unimportant (though here other, i.e. relativistic difficulties appear). In the presence of internal correlation, this is also true for models which take this, and no other, correlation fully into account. However, for smaller Z's, i.e. towards the neutrals, very large discrepancies systematically appear.

A new atomic structure theory with full inclusion of electron correlation, in a systematic way, for both ground and excited states developed recently by Sinanoğlu [2] has now given [3] for many such transitions, values accurate to 3–20% in close agreement with new experimental methods, which have been developed at the same time, such as beam-foil spectroscopy, phase-shift and new uses of the Hanle effect.

We shall show in the present note, in detail for Cl III $3s^2 3p^3(^4S^\circ) \to 3s3p^4(^4P)$, that a very large change in such transition probabilities can come from the inclusion of certain novel types of correlation effects found by NCMET [2] in both the upper and lower states. There are other methods, occasionally used in lighter atoms, for the calculation of allowed transition probabilities which go beyond the Hartree-Fock method. These are primarily the configuration-interaction method (sometimes called superposition of configurations (SOC)), the diagrammatic many-body perturbation theory (MBPT), and the many electron theory for ground and single determinantal states (MET) [4]. These approaches have been compared and discussed in some detail in the recent book by Sinanoğlu and Brueckner [5]. For detailed discussions of these, we refer the reader to that book. It is sufficient to note here that the conventional configuration interaction (SOC) method lacks a systematic way with which to choose the configurations to include. This of course, is natural as the method is not a physical theory of many electron effects, but an algorithm, like a series expansion, for expanding any function of a number of variables. Thus conventional attempts to improve wave functions by just adding configurations on the computer often miss physically significant configurations, while many configurations are added which can be shown by the theory (NCMET) to be unnecessary for properties like optical transition probabilities.

The MBPT as well as MET, on the other hand, are theories basically applicable to single determinantal states, i.e. ground states and also some states which are the lowest of their symmetry and still single determinantal. For many transitions, therefore, these methods can include correlation only on the lower states but not on the upper one. We shall show in the detailed analysis for the example below that this can lead to very serious errors in the oscillator strengths, sometimes greater than those of the Hartree-Fock method itself. In MBPT one also has the feature that the physically significant correlation effects are not given *a priori*, but higher orders of diagrams must be added on to achieve high accuracy. This is unlike the situation in Sinanoğlu's many electron theory (MET) approach for ground states [4] and the general Non-Closed Shell Many Electron Theory (NCMET) [2] for any excited state including those states which require multi-configurational Hartree-Fock wave functions.

In MET and NCMET the significant correlation effects have been predicted theoretically before any calculations and their role on various properties later confirmed.

The role of electron correlation in both the upper and lower states is most dramatic for the states so far considered [6] in the weaker ($f < 0.1$) transitions in the M-shells ($KLM \rightarrow KLM'$). In Table 1 we report our theoretical values for Cl III $KL\,3s^2 3p^3\,{}^4S^{\circ} \rightarrow KL\,3s3p^4\,{}^4P$, showing these effects. We give results of our calculations in which 1. both the lower and the upper states use restricted Hartree-Fock wave functions (the non-closed shell Hartree-Fock method), 2. the lower state includes all the non-closed shell type correlation effects, while the upper state stays as RHF, 3. the lower state is kept as RHF while only the upper state includes all the non-closed shell type correlation effects (NCMET) and finally 4. in which the full non-closed shell type wave functions of NCMET [2, 3] are used for both states.

We see in Table 1 that when the correlation is included in both states, the multiplet oscillator strengths (f_{E1}) drop from about 0.7 to about 0.09 [NCMET for both states], which is nearly a factor often.

The calculations have been performed with both the dipole r, and the dipole velocity ∇, operators. We note that the NCMET values for the two operators agree quite closely although such agreement, as seen in the RHF case, is necessary but not sufficient for accuracy.

In the calculations 2 and 3 in which only one of the states is correlated, we see very large discrepancies between the dipole length and the dipole velocity values. Further, the oscillator strength goes up and down in an erratic way. We have

Table 1. The Cl III $3s^2 3p^3 ({}^4S^{\circ}) \rightarrow 3s3p^4 ({}^4P)$ transition demonstrating the need for the inclusion of electron correlation in both the upper and lower states. The new atomic structure theory NCMET [8], now makes possible the inclusion of all of the non-closed shell correlation effects in both ground and excited states

Calculation[a]	Lower state (${}^4S^{\circ}$) wave function used	Upper state wave function used (${}^4P$)	f_r	f_{∇}
(1)	RHF	RHF	0.685	0.777
(2)[b, c]	NCMET – ψ_c	RHF	0.460	1.54
(3)[b]	RHF	NCMET – ψ_c	0.116	0.00186
(4)[b]	NCMET – ψ_c	NCMET – ψ_c	0.0855	0.1032

[a] All calculations (RHF and NCMET) are by the authors. The ε-experimental is used in both RHF and NCMET values.

[b] The ψ_c-calculations include all of the LM-shell non-closed shell correlations (1590 and 1676 Slater determinants).

[c] Note that although these correlations (ψ_c vs. ϕ_{RHF}) have very little effect on the energy of the ${}^4S^{\circ}$ state, they change the f_{E1} substantially.

observed similar effects of correlation in lower *and* upper states for other ($KLM \rightarrow KLM'$) transitions [6] and also in the lighter atoms involving $KL \rightarrow KL'$ transitions [2, 3].

The NCMET calculations and the basic theory have been described in detail elsewhere [6–8]. NCMET indicates that the exact wave function of any arbitrary non-closed shell state includes 4 distinct mutually-orthogonal parts: the Hartree-Fock wave function, the internal correlation wave function, the semi-internal plus orbital polarization wave function, and the all-external correlation wave function. The internal and semi-internal plus polarization correlations are strictly of the non-closed shell type. The latter having been found first by NCMET [8]. In the closed shell limit these correlations rigorously go to zero, the all-external correlations are the only ones that remain in a closed shell [4]. Thus, even in a complicated, non-closed shell state, the all-external correlations are essentially the closed shell-like correlations. Sinanoğlu has shown in NCMET [8] that they can be obtained in terms of the very same all-external pair correlations that occur in a strictly closed shell system like Ne atom. It has now been amply demonstrated that in certain properties such as the electric dipole transition probabilities [2] and some expectation values like the hyperfine structure constants [9], except the contact term, only the "charge distribution wave function" [7, 8] or "the charge wave function" for short, ψ_c, of NCMET is needed for quite high accuracy. Thus the charge distributions, or in the case of transitions, the transition charge densities are given well by just this charge wave function, ψ_c, which includes only the Hartree-Fock wave function, the internal, and the semi-internal and polarization correlations. Furthermore, it has been shown [7, 8] that these parts contain only a finite number of Slater determinants, their number and types determined essentially by group theory.

Fully automated computer programs Sinanoğlu and his co-workers have developed in the last several years, create all of these determinants, which are composed of the occupied and unoccupied Hartree-Fock spin-orbitals, and the new semi-internal orbitals of NCMET [6–8], and then carry out all the atomic algebra needed, before calculating the integrals and the coefficients needed.

Although in the KL shells, in atoms like C, N, O, the number of determinants for the charge wave functions of the L-shell were of the order of 20–80 or so, in the LM shells, such as in the Cl III example above, the determinants number 1590 in the lower state and 1676 in the upper state. Note that although these numbers are quite large, their number is still finite and determined *a priori* by the theory and furthermore in spite of the large size of such a calculation, the calculations take only a few minutes on the CDC 6600.

One may also note that the calculation of f_r and f_∇ involve the transition energy ε, which unlike the line strength, S, itself, should be calculated with the inclusion of both the charge correlations and the all-external correlation, because ε is not a charge-like property. NCMET gives either in purely non-empirical, or in theory guided, semi-empirical, ways [7] the all-external correlation energies as well. However, in most transitions the difference of the multiplet oscillator strengths, with and without the all-external energy added to ε differ only by about 3% (in the KL shells). Also, one can use the experimental ε whenever it is available and this is what is done in the calculation of Table 1 both for the

Hartree-Fock and for the NCMET calculations. Since in a quite accurate calculation, both f_r and f_∇ should and do agree with each other, one can also avoid using the ε altogether by simply using the geometric mean $\sqrt{f_r f_\nabla}$ in which ε does not appear. In connection with the detailed results shown on the Cl III example in Table 1, we also note that although the charge correlations have little effect on the energy of the $^4S^\circ$ state, they change the multiplet oscillator strength, f_{E1} substantially.

In concluding we note that it is necessary for consistently accurate theoretical transition probabilities, to include all the significant correlation effects in both the lower and the upper states. This seems to have been done systematically and with all the charge correlation effects included, for the first time in NCMET [2, 3, 8]. Other methods which by their nature include correlation in only one of the states could therefore lead to large errors.

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