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RELATIVISTIC EFFECTS IN THE CALCULATION OF OSCILLATOR STRENGTHS: "AB INITIO" METHODS

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Abstract - The methods used to introduce relativistic effects in the calculation of oscillator strengths are briefly reviewed. The main modifications induced by these effects are analyzed by considering some typical examples taken from recent calculations.

Introduction

Systematic studies [1,2] of the relativistic effects on atomic properties have pointed out that these effects are strongly dependent on the value of the orbital quantum number ℓ. Consequently it was expected that the calculation of oscillator strengths which involves radial matrix elements between two one-electron orbitals of different orbital quantum number, will be influenced, at least for heavy atoms, by the introduction of the relativistic effects. To be short let us just recall that the relativistic effects on the radial charge distribution can be divided into two contributions. The first one is due to the mass variation and the orthogonality constraints and results in a contraction of the charge density towards the nucleus when compared to non-relativistic results. Contrary to this effect which directly results from the use of the Dirac equation instead of the Schrödinger one, the second contribution is an indirect effect and is found only in self consistent calculations. Due to the more effective screening of the nuclear charge by the inner electrons, the charge density of the outer electrons tends to expand towards the outer region of the atom. It is obvious that these two effects will compete and that the net result on a given outer shell will greatly depend on the electronic configuration under consideration. For a more detailed study of the relative importance of these two contributions the reader is referred to the recent paper by Rose et al.[3]. Besides the obvious modification of the transition energy, the relativistic effects will also manifest themselves through the spin-orbit interaction in the sense that the states to be considered have now to be described in the intermediate coupling scheme and not in the Russell-Sanders one, consequently "spin forbidden" transitions no longer exist and they must be introduced in the description of the spectra.

Many recent theoretical works have been devoted to the study of relativistic effects on the calculations of oscillator strengths. These works may be classified according to the method used to perform the calculation but all of them show that the inclusion of the relativistic effects led to results which, along an isoelectronic sequence, largely deviate from the predictions of the non-relativistic results. In the first part of this paper we review the various methods used to perform these calculations with a particular emphasis of the more sophisticated completely ab initio methods. In the second part we will consider some typical examples to point out the modifications induced by the relativistic effects.

I. METHODS OF CALCULATION

Any relativistic calculation has to performed using some kind of approximated Hamiltonian since no exact one exist in a closed form, this point well discussed by Bethe and Salpeter [4] will not be considered here. The methods used up to now to introduce the relativistic effects in the calculations of oscillator strengths can be divided into two classes, one which is the relativistic counterpart of the Hartree-Fock method, time independent or not and a second one which makes use of model potentials. This latter one is discussed in detail in an other paper at this conference [5] and is just summarized here: a given form of the potential is assumed, this can be of the Slater...
type [6] or of some analytical form [7, 8]. When an analytical form is used, a certain number of parameters have to be determined according to various criteria, for example to minimize the energy [7] or to recover some known experimental results [8]. With this potential, which may or not be local or \( \xi \) dependent, a set of one-electron wavefunctions is generated. These wavefunctions are then used as basis functions to perform calculations at various order of the perturbation theory.

I.A. The Dirac-Fock method.

In the relativistic theory the only good quantum numbers are the total angular momentum \( J \) and the parity \( \pi \). States with the same \( J \) and \( \pi \) are further classified by the ordering of their energies. In its multiconfiguration version [9] the Dirac-Fock method proceeds as follows: a state of given total angular momentum \( J \) and parity \( \pi \) is written as a linear combination of wavefunctions having the same \( J \) and \( \pi \) quantum numbers but arising from different electronic configurations (in the relativistic case a configuration is defined in the \( jj \) coupling scheme):

\[
|J\pi> = \sum_i c_i |a_i J\pi>
\]

(1)

where \( a_i \) stands for all quantum numbers necessary to further specify the \( i^{th} \) configuration and \( c_i \) is the associated weight. In eq.(1) \( |a_i J\pi> \) are antisymmetric products of one-electron fourth order Dirac spinors. In the multiconfiguration method, both the radial functions of the Dirac spinors and the weighting coefficients \( c_i \) are determined self-consistently using the variational principle. The zero order hamiltonian used to perform self-consistent field calculations is, in all works reported up to now, restricted to the sum of one-electron Dirac operators plus the classical Coulomb repulsion between the electrons. After self-consistency has been achieved, the energy can be corrected by first order perturbation theory for higher relativistic effects (compared to those included in the one-electron Dirac hamiltonian), i.e.: magnetic interaction and retardation in the Coulomb interaction between the electrons, vacuum polarization and fluctuation. The influence of the magnetic interaction on the position of the fine structure levels will be discussed in the next section.

If in eq.(1) the electronic \( jj \) configurations included are restricted to those arising from a single \( LS \) non relativistic configuration, the multiconfiguration method is then used only to introduce completely ab initio the breakdown of the \( LS \) or \( jj \) coupling schemes. Stated in another way it means that the variational principle allows to determine wavefunctions in the intermediate coupling scheme. This point will be illustrated in the next section when considering the Beryllium isoelectronic sequence. If more than the above mentioned configurations are included, then some correlation effects are taken into account. As the multiconfiguration method utilize a variational principle to determine an optimum set of single particle wavefunctions, few configurations are generally required to give accurate results. For example in the Beryllium sequence [10], it was found that considering only the two configurations \( 1s^22s^2 \) and \( 1s^22p^2 \) for the ground state and the single \( 1s^22s2p \) excited configuration, multiconfiguration results only differ by relatively small amounts from those obtained by Burke et al.[11] in a correlation calculation including a total of 13 configurations.

1.B. The relativistic random phase approximation.

Although the random phase approximation (RPA) was originally developed for extended systems, its application to atomic processes had revealed quite successful especially for the calculation of transition probabilities and photoionization cross sections [12]. While in the multiconfiguration method described above one tries to optimize separately the wavefunctions of the initial and final states, the basic idea of the RPA approach is that one concentrates on the operator which connect initial and final states rather than on the states themselves. Approximations are then introduced either on the form of the operator or on the interactions restricted to belong to a given class of approximate wavefunctions. The RPA method can be viewed from three equivalent ways: the Green's function method [13], the linearized equations of motion method [14] and the time dependent Hartree-Fock theory [15]. The last approach has been used to develop the relativistic version of the random phase approximation [16] (RRPA). To summarize the RRPA let us just say
II. ILLUSTRATIVE EXAMPLES

The influence of relativistic effects on the calculation of oscillator strengths is illustrated by considering a few number of selected examples. The trends along an isoelectronic sequence are studied in the case of the beryllium sequence. We then consider the problem of level crossings due to the transition from LS to jj coupling scheme along a sequence. Finally the influence of high order relativistic corrections, mainly the magnetic interaction, on the fine structure level spacings is discussed.

II.A. The Beryllium sequence.

This sequence has been studied by various authors using either the multiconfiguration Dirac-Fock method (MCDF) [18,10] or the relativistic random phase approximation (RRPA) [19]. We discuss here the MCDF results which are in quite good agreement with the RRPA ones. As previously indicated, considering for the ground state the two $1s^22s^2$ and $1s^22p^2$ configurations and for the excited state the single $1s^22p^2$ configuration lead to accurate results. The ground state wavefunctions is expressed as:

$$\langle 1s \rangle^2 \left\{ a \langle 2s \rangle^2 + b \langle 2p_{1/2} \rangle^2 + c \langle 2p_{3/2} \rangle^2 \right\} \quad (2)$$

and in this case the MCDF method is used to introduce correlation effects due to the strong mixing between the two configurations as expected from the hydrogenic degeneracy of the $2s$ and $2p$ energy levels. In the relativistic case only the $2s$ and $2p_{1/2}$ levels are degenerated and the results given in Table I show, as expected, that the weight $b$ of the $(2p_{1/2})^2$ configuration remains essentially constant throughout the sequence while, due to the increase in the spin-orbit interaction, the contribution of the $(2p_{3/2})^2$ configuration decreases as the atomic number $Z$ increases. The influence of the spin-orbit interaction is also reflected in the variation of the ratio $(\gamma/b)^2$, for $Z = 10$ this ratio is almost equal to the non-relativistic value of 2 while for $Z = 74$ it has decreased to 0.04 and one has reached the jj coupling scheme limit.

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$(\gamma/b)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.968</td>
<td>0.147</td>
<td>0.205</td>
<td>1.94</td>
</tr>
<tr>
<td>42</td>
<td>0.966</td>
<td>0.141</td>
<td>0.089</td>
<td>0.40</td>
</tr>
<tr>
<td>54</td>
<td>0.989</td>
<td>0.138</td>
<td>0.054</td>
<td>0.15</td>
</tr>
<tr>
<td>74</td>
<td>0.992</td>
<td>0.126</td>
<td>0.024</td>
<td>0.04</td>
</tr>
</tbody>
</table>

For the excited state the wavefunction is given by:

$$\langle 1s \rangle^2 \left\{ \sqrt{1-a^2} \langle 2s 2p_{3/2} \rangle^2 - a \langle 2s 2p_{1/2} \rangle^2 \right\} \quad (3)$$

The non-relativistic allowed transition is associated with the $^1P_1$ state for which $a = 0.577 \sqrt{2/3}$. In the relativistic case and for the low Z-region this state is found to be the upper $J = 1$ eigenstate while the lower one corresponds to the $^3P_1$ state. As seen from the results given in
Table II, the value of the "a" coefficient rapidly deviates from the LS limit and for high Z-ions one reaches the jj coupling limit. It is clear from the results we have just discussed that the intermediate coupling scheme must be introduced to obtain accurate results either by the relativistic variational approach we have described or by a suitable perturbation method.

Table II
Second J = 1 state of the Be sequence
"a" coefficient of Eq.3

<table>
<thead>
<tr>
<th>Z</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.572</td>
</tr>
<tr>
<td>42</td>
<td>0.200</td>
</tr>
<tr>
<td>54</td>
<td>0.102</td>
</tr>
<tr>
<td>74</td>
<td>0.038</td>
</tr>
</tbody>
</table>

When plotted as a function of Z, the relativistic results for the dipole oscillator strengths (f values) display a quite different behaviour than the one obtained in the non-relativistic case. While the latter one gives a monotonically decreasing function of Z, the f values obtained in the relativistic calculations show, for the beryllium sequence, a minimum around Z = 35 and then begin to increase with Z. Furthermore, starting from Z = 20 the relativistic f values are significantly larger than the non-relativistic ones and are in better agreement with the recommended values of Smith and Wiese [20]. To analyze the relativistic effects, it is convenient to consider separately the two factors contributing to the f value, i.e. the excitation energy E and the line strength S. In term of these, f is defined in the length form as:

\[ f = E S (3gR)^{-1} \]

(4)

where R = 13.6 eV and g is the degeneracy of the initial state. Results for E, S and f are given in Table III for selected Z values of the beryllium sequence. It can be seen that, in the relativistic case, E increase much more rapidly with Z while S remains close to the non-relativistic value throughout the sequence. This again reflects the influence of the spin-orbit interaction since, for the Z-region, the excited state is almost purely the J = 1 state of the single sp\(^{3/2}\) configuration.

Table III
f values for the beryllium sequence

<table>
<thead>
<tr>
<th>Z</th>
<th>E(eV)</th>
<th>Z^2S</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R</td>
<td>NR</td>
<td>R</td>
</tr>
<tr>
<td>10</td>
<td>28.31</td>
<td>28.10</td>
<td>57.44</td>
</tr>
<tr>
<td>42</td>
<td>251.9</td>
<td>136.0</td>
<td>40.16</td>
</tr>
<tr>
<td>74</td>
<td>1758.</td>
<td>243.0</td>
<td>33.80</td>
</tr>
</tbody>
</table>

R and NR stand for relativistic and non-relativistic results E and S are the transition energy and the line strength as defined by Eq.3.

For transitions to the lowest J = 1 state (corresponding to the \(^3\)P\(_1\) state for the low Z-region) it was found that the f values are smaller by a factor of 10\(^3\) (low Z-ions) to 20 (high Z-ions) compared to the "allowed" transition to the upper state. Thus the "forbidden" transition remains weak even in the jj coupling limit for the beryllium like ions. Similar results where found for the magnesium sequence [17,12] and discussed in terms of the relativistic Z-dependent theory of many-electron atoms [22]. Non monotonous decrease of the f values with the atomic number Z where also reported for the lithium [10,18] and sodium [23] isoelectronic series.

II.B. Level crossings.

In this section we want to discuss an other consequence of the transition from LS to jj coupling scheme, i.e. the fact that the level ordering changes between low Z and high Z-region. As an example let us consider the case of the magnesium sequence studied by Cheng and Johnson [21].

The first four eigenstates with even parity and having J = 2 as total angular momentum eigenvalue arise from the \((3s)^2\) and \((3s3d)\) configurations. For low Z-values when the spin-orbit interaction is negligible, the ordering of these levels was found to be: \((3p)^2 1\text{D}_2\), \((3p)^2 3\text{P}_2\), \((3s3d)^2 3\text{D}_2\) \((3s3d)^2 3\text{P}_2\). Then spin-orbit interaction is dominant, the ordering of the \((jj')\) levels follows the following sequence: \((1/2 1/2), (1/2 3/2), (1/2 5/2), (3/2 3/2)\) ... Thus since in the jj coupling limit, the \((3s3d 3/2)\) state is lower in energy than the \((3p 3/2)\) state, these two states have to cross at some value of the atomic number Z. Even if true crossings are forbidden, the previous consideration implies that, for some given values of Z, the two levels...
will be very close in energy from each other and consequently strong interaction between them will take place. Such a strong interaction will result in a decrease of the transition probability due to destructive interference between the transition channels or to the enhancement of the transition caused by coherent mixing. For the Mg sequence it was found that such a situation arises around \( \text{Z} \approx 45 \) and that the mixing of the \((3p)^2 \) and \((3s3d)\) configurations in the \(3p_2\) state strongly suppresses, in the high \( \text{Z} \)-region, the transitions to the \(3p_2\) and \(1p_1\) states of the \((3s3p)\) configuration while the transition to the \(3p_1\) state was enhanced.

Except for very simple configurations, level crossings are likely to happen and will result in irregularities in the line strengths. It is therefore important to consider with great care the regions of possible level crossings when looking at systematic trends in the transition probabilities.

II.C. Fine structure splittings.

As mentionned in I, the zero order hamiltonian, used, in the HCDF method to determine the wavefunctions, includes only the spin-orbit interaction which is explicitly taken into account in the Dirac one-particle hamiltonian. The spin-spin and spin-other-orbit interactions, which come from the Breit operator, are treated as a first order perturbation and often calculated in the average configuration approximation \cite{24,25}. If the electrons belong to closed shells or at most only one is in an open shell, the configuration averaging provides the exact contribution but for general open shells systems it is only an approximation.

Recent experimental results \cite{26} have shown substantial deviations from the Landé rule in the intervals of the fine structure levels and theoretical calculations \cite{27} have been carried out to assess the reliability of "ab initio" methods. It was found that the Breit interaction plays a crucial role to obtain good agreement with experiment and that the configuration averaging was a poor approximation in the cases under consideration.

For the fine structure splittings in the \(1s^2p^2(^4\text{P})\) and \(1s^22s2p(^4\text{P})\) states of lithium ions three successive approximations were used. First the Breit interaction was completely neglected, in this case the fine structure intervals were found to follow closely the Landé rule as expected since only the spin-orbit interaction was included. Secondly the Breit interaction was calculated in the configuration average contribution. Compared to the first case, a general shift of the energy levels was observed but with almost no change in the spacing between them. Finally the magnetic part of the Breit term was calculated correctly and dramatic changes in the fine structure occurred. At this stage, agreement with experiment is of the order of 10\% and the remaining discrepancy should be reduced if the retardation part of the Breit operator and other quantum electrodynamic effect (vacuum polarization and fluctuation) are also correctly taken into account.

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