A sum rule for ionization potentials, similar to the Manne–Aberg theorem, is derived in the framework of a many-body Green's-function formalism. This sum rule is shown to be valid under mainly two conditions: (i) the constant term and the affinity poles of the self energy part have to be neglected; and (ii) the final state wavefunction has to be separable in a free-electron and an \((N-1)\)-electron part. The latter assumption is discussed in connection with the sudden approximation which is not used for the derivation of the new sum rule.

I. Introduction

In its most simple form the one-particle picture leads to a one-to-one correspondence of observable ionization processes and occupied orbitals. Due to Koopmans' theorem [1] the ionization potentials \(I_{k}^{(0)}\), which correspond to these processes, are approximated by
\[
I_{k}^{(0)} = -\epsilon_{k}.
\] (1)

Satellite structures, often observed in connection with inner shell ionization [2] are not compatible with this simple picture. In the one-particle scheme these satellites with ionization potentials \(I_{k}^{(n)}\) and relative intensities \(t_{k}^{(n)}\), the intensity of satellite/ intensity of "main peak", are interpreted as single and multiple excitations accompanying the electron emission.

The loss of the above-mentioned one-to-one correspondence was restored to some extent by Manne and Aberg [3]. These authors introduced a sum rule in which \(I_{k}^{(0)}\) is replaced by a weighted average over different final states
\[
-\epsilon_{k} = I_{k}^{(0)} + \sum_{n \neq 0} \langle \Psi_{n}^{N-1} | \Psi_{k}^{N-1} \rangle^{2} (I_{k}^{(n)} - I_{k}^{(0)}).
\] (2)

Here the square of the matrix element, which is the projection of the ion-state wavefunction \(|\Psi_{n}^{N-1}\rangle\) on the Koopmans-state \(|\Psi_{k}^{N-1}\rangle\), corresponds to the relative intensity \(I_{k}^{(n)}\) of the satellite line (it should be mentioned that the "main peak" with IP \(I_{k}^{(0)}\) is not always related to the peak with the largest observed intensity). Eq. (2) was derived under the following two approximations:

(i) Application of the sudden approximation and separation of the final state wavefunction in a free-electron and an \((N-1)\)-electron state. These different approximations are often thought to be completely equivalent (see below).

(ii) Assumption of constant one-electron transition moments.

Due to the latter approximation (ii) the resulting transitions are supposed to be controlled by monopole selection rules.

Manne and Aberg [3] explicitly state in their paper that the sudden approximation is not applicable to cases where the energy of the exciting radiation is close to threshold, and for ionizations from the valence shell. This is in line with a detailed comparison of the sudden versus adiabatic approximation by Meldner and Perez [4] who arrive at the conclusion that whenever the sudden approximation is appropriate the ionized system is probably "shaken", while in the limit of the adiabatic approximation the system ends up in a single eigenstate of the ion. From this it was suggested that one has not to expect considerable satellite structure in UPS spectra. Recent experiments, however,
on small molecules using He(II) excitation have revealed strong satellite structures in the region of inner valence shell ionization [5]. These structures could be well interpreted in terms of many-particle effects using a theory which is mainly based on a Green's-function formalism [6-8]. As this formalism is essentially based on the adiabatic approximation [9] the question arises, whether a sum rule similar to the Manne-Åberg theorem [3] can also be derived for the valence shell region. In connection with the discussion of the extended Koopmans theorem [10], Pickup [11] already indicated that in the framework of the superoperator formalism, a similar sum rule may be derived.

2. Formalism

We start here with the well-known expression for the one-particle Green's function

\[ G_{pq}(\omega) = \sum_n \frac{X_p^{(n)} X_q^{(n)}}{\omega - I_n - i\epsilon} + \sum_m \frac{Y_p^{(m)} Y_q^{(m)}}{\omega - A_m + i\epsilon} , \]  

(3)

with

\[ X_p^{(n)} = \langle \Psi_n^{-1} | a_p | \Psi_0 \rangle , \quad Y_p^{(m)} = \langle \Psi_0 | a_p | \Psi_m^{N+1} \rangle , \]

using the usual nomenclature [12]. The ionization potentials \( I_n \) and electron affinities \( A_m \) are found via the inverse Dyson equation. Numerically they are evaluated in good approximation to the exact results by assuming \( G \) to be diagonal [7,13]. In the case of diagonal \( G \) the IP's \( I_n^{(n)} \) are related to the negative roots of

\[ \omega - \epsilon_k - \Sigma_{kk}(\omega) = 0 . \]  

(4)

The corresponding relative intensities \( t_k^{(n)} \) are given by

\[ p_k^{(n)} = X_k^{(n)} X_k^{(n)} = |\langle \Psi_n^{-1} | a_k | \Psi_0 \rangle|^2 . \]  

(5)

To derive these results, two approximations have been used which are the same as in the treatment of Manne and Åberg:

(i) A separation-ansatz is used for the final state wavefunction.

(ii) The one-electron transition moments are taken to be constant.

Following Cederbaum [14], the exact self-energy part can be written as

\[ \Sigma_{kk}(\omega) = A_{kk} + \sum_j \frac{V_j^2}{\omega - K_j} + \sum_j \frac{W_j^2}{\omega - L_j} , \]  

(6)

where \( K_j \) is the ionization pole of \( \Sigma \) and \( L_j \) the affinity pole of \( \Sigma \). For numerical applications the constant term \( A_{kk} \) is set equal to zero.

By complete induction the evaluation of the roots of eq. (4) is equivalent to diagonalisation of the following matrix \( M_k \):

\[
\begin{bmatrix}
\epsilon_k & V_j & \cdots & W_j \\
0 & \ddots & \ddots & \ddots \\
\vdots & \ddots & \ddots & \ddots \\
W_j & 0 & \cdots & L_j \\
0 & \cdots & \ddots & \ddots
\end{bmatrix}
\]  

(7)

If one starts from a CI-variation ansatz

\[ |\Psi_n^{N-1} \rangle = \left[ c_0^{(n)} a_k + \sum_{jml} c_m^{(n)} a_j^{(m)} a_m a_l \right] |\Psi_{\text{HF}} \rangle \]  

(8)

a matrix can be derived [15] which is identical to the upper left block of the matrix \( M_k \). This shows that the ansatz (8) leads to the neglect of the influence of the \( L_j \) and \( W_j \) on \( \epsilon_k \) (which is equivalent to a complete neglect of ground-state correlation [15]). In adopting this approximation we use a completely uncorrelated ground state and restrict our further discussion to the submatrix \( M_k^{\text{sub}} \). It then follows from eqs. (5) and (7) that

\[ p_k^{(n)} = |c_0^{(n)}|^2 , \]  

(9)

with the normalization condition

\[ \sum_n p_k^{(n)} = 1 . \]  

(10)

If the \( n \)th eigenvalue of \( M_k^{\text{sub}} \) is denoted \( E_k^{(n)} \) it follows that

\[ \epsilon_k = \sum_n p_k^{(n)} E_k^{(n)} . \]  

(11)

Insertion into eq. (10) leads, together with eq. (5), to

\[ \epsilon_k = E_k^{(0)} - \sum_{n \neq 0} \langle \Psi_n^{N-1} | a_k | \Psi_{\text{HF}} \rangle (E_k^{(n)} - E_k^{(0)}) , \]  

(12)
a result which is completely equivalent to the Manne–Åberg theorem [3]. Evidently a similar formula is valid for electron affinities if the influence of the ionization poles is neglected. It should be mentioned at this point that the special type of configurations which are included in the CI ansatz (8) have not been used to obtain the above expression.

The equivalence between our results and those of Manne and Åberg are mainly induced by two approximations:

(i) The constant term and the affinity poles of the self-energy part are neglected.

(ii) The final-state wavefunction is separated into a free-electron wavefunction and a wavefunction for the $(N-1)$-electron system.

Without doubt the first approximation is justified for core ionizations where the energy difference between $e_K$ and $I_f$ is always large. For valence-shell ionizations its applicability depends to some extent on the magnitude of the HOMO–LUMO gap, but for the inner part of the valence shell it is certainly not too bad.

The more important approximation is the second one. Physical intuition suggests a strong connection between the separability of the final-state wavefunction and the sudden approximation: The separation is the more reliable the higher the energy of the emitted particle is and the sudden approximation is the better the faster the perturbation takes place. As a consequence, it is often assumed that the separation is inherent in the sudden approximation. From the formalistic point of view this is, however, not true. The sudden as well as the adiabatic approximation is defined via the time evolution of the hamiltonian [4, 16] which does not necessarily lead to a separation of the final state wavefunction. Consequently, this separation has to be introduced as an independent assumption. The similarity of results derived either in the framework of the sudden or in the framework of the adiabatic approximation, as shown in this letter, clearly reveals that it is not the special type of perturbation theory which is responsible for these results but the common assumption of a separable final-state wavefunction. For further investigations it should be attended more precisely that this latter assumption is not directly connected with the sudden approximation.

References