

CONNECTION BETWEEN THE MANNE-ÅBERG THEOREM AND A SUM RULE DERIVED IN THE FRAMEWORK OF THE GREEN'S-FUNCTION FORMALISM

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Received 6 August 1979; in final form 17 September 1979

A sum rule for ionization potentials, similar to the Manne-Åberg 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; (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.

1. 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

$$I_k^{(0)} = -\epsilon_k. \quad (1)$$

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 Åberg [3]. These authors introduced a sum rule in which $I_k^{(0)}$ is replaced by a weighted average over different final states

$$-\epsilon_k = I_k^{(0)} + \sum_{n \neq 0} \langle \Psi_n^{N-1} | \Psi_k^{N-1} \rangle^2 (I_k^{(n)} - I_k^{(0)}). \quad (2)$$

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 Åberg [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 super-operator 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

$$G_{pq}(\omega) = \sum_n \frac{X_p^{(n)} X_q^{(n)}}{\omega - I_n - i0^+} + \sum_m \frac{Y_p^{(m)} Y_q^{(m)}}{\omega - A_m + i0^+}, \quad (3)$$

with

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

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 $I_k^{(n)}$ are related to the negative roots of

$$\omega - \epsilon_k - \Sigma_{kk}(\omega) = 0. \quad (4)$$

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

$$p_k^{(n)} = X_k^{(n)} X_k^{(n)} = |\langle \Psi_n^{N-1} | a_k | \Psi_0 \rangle|^2. \quad (5)$$

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

$$\Sigma_{kk}(\omega) = A_{kk} + \sum_j \frac{V_j^2}{\omega - K_j} + \sum_j \frac{W_j^2}{\omega - L_j}, \quad (6)$$

where K_j is the ionization pole of Σ and L_j the affinity pole of Σ . 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 :

$$M_k = \begin{bmatrix} \epsilon_k & \dots & V_j & \dots & \dots & W_j & \dots \\ \vdots & \ddots & & 0 & & & \\ V_j^* & & K_j & & & & 0 \\ \vdots & & & \ddots & & & 0 \\ W_j^* & & 0 & & & L_j & \\ \vdots & & & & 0 & & \ddots \end{bmatrix} \quad (7)$$

If one starts from a CI-variation ansatz

$$|\Psi_n^{N-1}\rangle = \left[c_0^{(n)} a_k + \sum_{jml} c_{jml}^{(n)} a_j^+ a_m a_l \right] |\Psi_{\text{HF}}\rangle. \quad (8)$$

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 ϵ_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^{sub} . It then follows from eqs. (5) and (7) that

$$p_k^{(n)} = |c_0^{(n)}|^2. \quad (9)$$

with the normalization condition

$$\sum_n p_k^{(n)} = 1. \quad (10)$$

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

$$\epsilon_k = \sum_n p_k^{(n)} E_k^{(n)}. \quad (11)$$

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

$$\epsilon_k = E_k^{(0)} - \sum_{n \neq 0} \langle \Psi_n^{N-1} | a_k | \Psi_{\text{HF}} \rangle (E_k^{(n)} - E_k^{(0)}), \quad (12)$$

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 ϵ_k and L_j 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.

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