Effect of correlations on the photoelectron spectrum of the atom

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The self-energy part of the quasihole Green function of an atom is used to calculate the spectral density of photoelectrons with allowance for many-electron correlations. A number of relationships is established between the Hartree-Fock and exact energies of quasihole states and the intensities of the corresponding photoelectron peaks. It is shown that allowance for many-electron correlations does not affect the resultant intensity or the "center of gravity" of the photoelectron spectrum.

1. INTRODUCTION

Certain general properties of the photoelectron spectrum of an atom that are due to correlation effects will be established in this paper. In the single-particle approximation, the photoelectron spectrum consists of individual peaks, each of which is associated with the ionization of a particular atomic shell. Many-particle effects produce a considerable complication of the photoelectron spectrum, so that a single-particle peak becomes transformed into a set of discrete lines and a continuous band.

If many-particle effects are taken into account by modifying the Hartree-Fock self-consistent field, the "center of gravity" of the many-particle spectrum occurs at the binding energy of the removed electron, and its resultant intensity is equal to the intensity of the corresponding single-particle peak.[1] It will be shown below that this result is quite general. It does not rely on the features of the Hartree-Fock approximation, and remains valid when account is taken of the direct interaction between the electrons, i.e., of many-electron correlations.

We shall take these correlations into account by using the many-body formalism in which the removal of an electron from an atom is looked upon as the production of a quasihole in the ground or excited state of the system. Generally speaking, the energies of the quasihole excitations differ from the energy of the ith ionized shell, and can be found as the poles of the quasihole Green function $G_i(\varepsilon)$, regarded as a function of the binding energy.[2] This involves the solution of Dyson's equation with the self-energy part $\Sigma_i(\varepsilon)$ of the Green function, which can be found by summing the perturbation-theory series over the interelectron interaction.

The binding energy region in which $\Sigma_i(\varepsilon)$ is complex determines the continuous band in the photoelectron spectrum. For binding energies for which $\Sigma_i(\varepsilon)$ is real, the photoelectron spectrum consists of discrete lines that correspond to the poles of $G_i(\varepsilon)$. The line intensity is proportional to the residues of $G_i(\varepsilon)$ at these poles.[3]

The effect of electron correlations on the photoelectron spectrum can be taken into account by including them in the self-energy part. In Section 2, we obtain an expression for $\Sigma_i(\varepsilon)$ in the first nonvanishing order of small quantities in the interelectron interaction, which corresponds to the inclusion of simple correlations in the atom, namely, the virtual decay of the Hartree-Fock hole into two other holes and an excited electron. In this approximation $\Sigma_i(\varepsilon)$ can be represented by the sum of individual terms, each of which corresponds to a virtual transition to an intermediate state of two holes plus one electron, and an integral over the continuous spectrum of these states. We shall show that this representation of $\Sigma_i(\varepsilon)$ is a consequence of the Lehman expansion for Green's function, and is valid when correlation corrections of any degree of complexity are introduced.

In Section 3, we investigate the analytic properties of Green's function and the spectrum of quasihole states. We show that the shape of this spectrum depends on whether the Hartree-Fock hole is capable of real decay. When decay does not occur, the quasihole ground state lies above the energy of the Hartree-Fock hole. Excited quasihole levels correspond to discrete virtual states over which the expansion of $\Sigma_i(\varepsilon)$ is performed (in the simplest case, these are states of the form two holes plus one electron) and lie below the Hartree-Fock energies of the corresponding virtual states. When real decay becomes possible, the Green-function pole that previously corresponded to the quasihole ground state is found to appear in the complex plane of the binding energy of its nonphysical sheet. All the quasihole levels, including the ground state, are then determined by discrete intermediate states in the expansion of $\Sigma_i(\varepsilon)$, and their energies lie above the corresponding Hartree-Fock energies. It will be shown that, in both cases, the sum of the Hartree-Fock energies of the "bare" hole and the discrete intermediate states is equal to the sum of the energies of the quasihole levels.

The theory of functions of a complex variable will be used to show that the residues of Green's function $G_i(\varepsilon)$ and also the products of the residues by the energy of the corresponding quasihole states satisfy simple sum rules. In Section 4, we shall obtain an expression for the spectral density of photoelectrons, which takes into account many-electron correlations. It follows from this expression that the relationships obtained in Section 3 can be interpreted as an equation between the integrated intensity of the multiparticle spectrum and the intensity of the corresponding single-particle peak, and as a correspondence between the center of gravity of the multiparticle spectrum and the Hartree-Fock binding energy of the electron that is being removed. The validity of these results will be illustrated by the photoelectron spectrum of the 3s shell of the argon atom.

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2. GREEN'S FUNCTION FOR A QUASIHOLE

We shall suppose that, in the absence of correlations, the hole can be described by a single-electron wave function of an occupied state in the self-consistent field of the atom (bare or Hartree-Fock hole). The Green function for this hole is diagonal in the basis of single-particle Hartree-Fock wave functions. The diagonal matrix element is given by

$$G_i^0(\varepsilon)=(\varepsilon-w_i)^{-1}, \tag{1}$$

where w_i is the Hartree-Fock energy of the hole.

Inclusion of many-electron correlations corresponds to the introduction of an interaction between the hole and other more complicated states, for example, two holes plus one electron. Instead of the isolated hole, we must speak of a quasihole excitation in the atom and a quasihole Green function.

The exact Green function of a quasihole will not, in general, be diagonal in the basis of the Hartree-Fock single-particle wave functions. If we suppose, however, that the energies of the atomic shells are essentially different, and correlations do not appreciably modify the shell structure, we can neglect the off-diagonal matrix elements. The exact Green function is thus assumed to be diagonal:

$$G_i(\varepsilon)=(\varepsilon-w_i-\Sigma_i(\varepsilon))^{-1},$$

where $\Sigma_i(\varepsilon)$ is the diagonal matrix element of the self-energy part.

As noted in the Introduction, the matrix element $\Sigma_i(\varepsilon)$ can be evaluated by summing the perturbation theory series over the interelectron interaction. The first nonvanishing terms in the expansion of $\Sigma_i(\varepsilon)$ correspond to the virtual creation of an additional particle-hole pair, and are illustrated graphically in Fig. 1. We use the usual symbols of the diagram method of the many-body formalism: a straight line with an arrow pointing to the right represents an electron in the Hartree-Fock field, either in a vacant level or in the continuous spectrum, whereas an arrow pointing to the left represents a Hartree-Fock hole; a wave line represents the Coulomb interaction between the electrons. The indices l, m, k represent the set of quantum numbers defining the single-particle state.

If we confine our attention to the diagrams of Fig. 1, we obtain the following expression:

$$\Sigma_i(\varepsilon)=S\sum_{k}\sum_{l,m}\frac{|\langle ik|V|lm\rangle+\langle ik|V|ml\rangle|^2+3|\langle ik|V|lm\rangle-\langle ik|V|ml\rangle|^2}{\varepsilon-w_m-w_l+w_k} \tag{2}$$

where the symbol S represents summation over discrete states of the excited electron k and integration over the continuous spectrum, and $\langle ik\,|V|\,lm\rangle$ is the Coulomb matrix element. The expression in the numerator includes summation over the spins of the particles and holes in the intermediate state, and w_l, w_m, w_k are the energies of the corresponding Hartree-Fock single-particle states.

FIG. 1

The hole states l, m will be considered as given, and this will result in a considerable simplification of the derivation. All results obtained in this way are readily generalized to the case of an arbitrary number of hole states.

Let us denote the energy of the intermediate state in the form of two holes and one particle, as follows:

$$w_l+w_m-w_k=\begin{cases}E_k, & w_k<0\\ \varepsilon', & w_k>0\end{cases}.$$

Expression (2) can then be written in the form

$$\Sigma_i(\varepsilon)=\sum_{k=1}\frac{a_k}{\varepsilon-E_k}+\int_{-\infty}^{E_\infty}\frac{a(\varepsilon')}{\varepsilon-\varepsilon'}d\varepsilon', \tag{3}$$

where the positive coefficients a_k, $a(\varepsilon')$ are expressed in terms of the Coulomb matrix elements. Moreover, $E_\infty=w_l+w_m$ is the limit of the continuous spectrum. The sum in (3) is evaluated over an infinite number of terms, since the wave function of the excited electron k is calculated in the field of the ion, whose asymptotic behavior at infinity is $1/r$. The discrete spectrum of the states k has a condensation point. It can be shown that, at the threshold, the discrete spectrum passes continuously into the continuous spectrum in the limit as $k\to\infty$:

$$\lim_{k\to\infty}\frac{a_k}{\Delta E_k}=\lim_{k\to\infty}\frac{a_k}{E_{k+1}-E_k}=a(E_\infty). \tag{4}$$

3. ANALYTIC PROPERTIES OF GREEN'S FUNCTION

We shall show that the structure of the expression for the self-energy part $\Sigma_i(\varepsilon)$ in (3) determines the nature of the spectrum of quasiholes. The explicit form of the coefficients a_k, $a(\varepsilon')$ and energies E_k is then unimportant. We shall also show that the structure of expression (3) for the self-energy part remains unaltered when correlations of any degree of complexity are taken into account. At the same time, the use of the diagrams in Fig. 1 enables us to find the explicit expression for the parameters in (3), which is essential for numerical calculations.

The spectrum of the quasihole states is determined by the poles of Green's function, which need not lie on the real axis. We must therefore determine the Green's function for the entire complex plane of the binding energy. This will be done by first examining its behavior on the real axis, and then constructing the analytic continuation into the complex plane.

We shall omit the subscript i on the functions $G_i(\varepsilon)$ and $\Sigma_i(\varepsilon)$, when we employ the corresponding matrix elements. The Hartree-Fock energy of the initial hole w_i will be denoted by E_0. Moreover, it will be convenient to consider the function

$$F(\varepsilon)=G^{-1}(\varepsilon)=\varepsilon-E_0-\Sigma(\varepsilon),$$

whose roots lie at the poles of $G(\varepsilon)$.

Consider the behavior of $F(\varepsilon)$ on the axis $\mathrm{Im}\varepsilon=0$. On the segment $\varepsilon>E_\infty$, the function $F(\varepsilon)$ is real. The points E_k

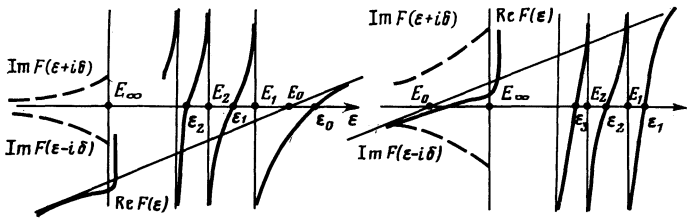

FIG. 2

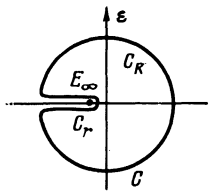

FIG. 3

are simple poles of $F(\varepsilon)$. The function $F(\varepsilon)$ has a discontinuity at each of these points and experiences a change of sign. At the continuous spectrum limit, $F(E_\infty)$ is finite. Although the integral in (3) diverges logarithmically, we can show by using the continuity condition (4) that, as $\varepsilon \to E_\infty - 0$, the diverging part of the integral is cancels with the infinite sum over the discrete spectrum. On the segment $\varepsilon < E_\infty$, the integral in (3) must be interpreted as meaning its principal value. Accordingly, the function $F(\varepsilon)$ can be defined as the limit $F(\varepsilon \pm i\delta)$ as $\delta \to 0$. At infinity, $F(\varepsilon) \to \varepsilon - E_0$, since $\Sigma(\varepsilon) \to 0$ as $\varepsilon \to \pm\infty$. Figure 2 shows the graph of $F(\varepsilon)$ on the real axis.

The roots of $F(\varepsilon)$ on the segment $\varepsilon > E_\infty$ are the poles of the Green function. On the segment $\varepsilon < E_\infty$, the function $F(\varepsilon)$ has a nonzero imaginary part, so that the roots of $\mathrm{Re}F(\varepsilon)$ are not the poles of $G(\varepsilon)$. It is clear from Fig. 2 that the behavior of $F(\varepsilon)$ for $\varepsilon > E_\infty$ is determined by the ratio of the Hartree-Fock energies E_0 and E_k. When $E_0 > E_i$, i.e., the original hole cannot actually decay into two other holes and an electron, the function $S(\varepsilon)$ has a root $\varepsilon_0 > E_0$ (quasihole ground states). Moreover, for each discrete state k, there is a root $E_{k+1} < \varepsilon_k < E_k$. Thus, the number of real roots of $F(\varepsilon)$ is greater by one than the number of poles (Fig. 2a). On the other hand, when $E_0 < E_\infty$, i.e., real decay of the hole is possible, the root ε_0 falls into the regions where $\mathrm{Im}F(\varepsilon) \neq 0$, and is not a pole of $G(\varepsilon)$. For each discrete state k, there is, as before, one root E_k, but now $E_{k-1} > \varepsilon_k > E_k$ (Fig. 2b).

Let us now consider the analytic continuation of $F(\varepsilon)$ into the complex plane. To do this, we introduce a cut along the half-axis $\varepsilon < E_\infty$. From the upper edge of the cut, we continue $F(\varepsilon)$ into the upper half-plane and, from the lower edge, into the lower half-plane. Since the cut is introduced along the half-axis, we can choose a contour that connects the two edges of the cut. Hence, the analytic continuation determines unambiguously the function $F(\varepsilon)$ on the entire complex plane.

We showed above that the number of roots of $F(\varepsilon)$ on the real axis is either equal to or exceeds by one the number of poles. We shall now show that $F(\varepsilon)$ has no other roots. We shall use the well-known relation between the number N of zeros and the number P of poles of the function $F(\varepsilon)$ in the interior of a contour C (Ref. 4):

$$N-P=\frac{1}{2\pi}\int_C \frac{F'(\varepsilon)}{F(\varepsilon)}\,d\varepsilon=\frac{1}{2\pi}\int_{C'} d(\arg F(\varepsilon)).$$

Let us take the contour C in the complex plane of the binding energies as shown in Fig. 3. The radius of the large circle C_R will be allowed to tend to infinity, and that of the small circle C_r to zero. The contour C', which is a mapping of C by the function $F(\varepsilon)$, can readily be constructed with the aid of Fig. 2. This contour is shown in Fig. 4a (for $E_0 > E_1$) and in Fig. 4b (for $E_0 < E_\infty$). The increase in the argument of the function $F(\varepsilon)$ along the contour C' is either 0 or 2, depending on the ratios of E_0, E_1, and E_∞, and corresponds to the number of zeros and polees of $F(\varepsilon)$ on the real axis. We have thus shown that all the roots of $F(\varepsilon)$ are real.

If we continue $F(\varepsilon)$ from the upper edge of the cut to the lower half-plane, we obtain the nonphysical branch of the function $F(\varepsilon)$ and, correspondingly, the unphysical branch of the Green function. Similarly, it can be shown that, when $E_0 < E_\infty$, the unphysical branch of the Green function acquires two additional complex-conjugate poles.

We shall now establish the relationship between the energies E_k of intermediate states, over which the expansion of $\Sigma(\varepsilon)$ is performed, and the energies ε_k of the quasihole levels. We shall use the relationship between the sum of roots and poles of the function $F(\varepsilon)$ that lie inside the contour C (Ref. 4):

$$\sum_{k=0}^{\infty}\varepsilon_k-\sum_{k=1}^{\infty}E_k=\frac{1}{2\pi}\int_C \varepsilon\frac{F'(\varepsilon)}{F(\varepsilon)}\,d\varepsilon.$$

To be specific, we shall consider the case where $E_0 > E_1$ and the sum $\Sigma_k \varepsilon_k$ begins with zero. The integral over C_R yields E_0, whilst the integral over C_r is zero. A circuit around the cut is equivalent to repeated integration along the half-axis $\varepsilon < E_\infty$ in different directions. Since, on different edges of the cut, the real parts of $F(\varepsilon)$ are equal, whereas the imaginary parts have opposite signs, we obtain

$$\sum_{k=0}^{\infty}(\varepsilon_k-E_k)+\frac{1}{\pi}\int_{-\infty}^{E_\infty}\varepsilon\frac{\partial}{\partial\varepsilon}\arg F(\varepsilon)\,d\varepsilon=0. \qquad (5)$$

We must now establish the expression for the sum of residues of the Green's function of a quasihole at its poles. We shall use the Cauchy residue theorem:[4]

$$\frac{1}{2\pi i}\int_C G(\varepsilon)\,d\varepsilon=\sum_{k=0}^{\infty}z_k.$$

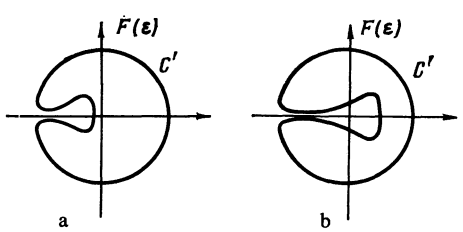

FIG. 4

The contour C will be the same as before (Fig. 3). The integral over C_R yields unity, whilst that over C_r yields zero. A circuit along the cut reduces to an integral over the real half-axis. The final result is

$$\sum_{k=0}^{\infty} z_k + \frac{1}{\pi}\int_{-\infty}^{E_\infty} \frac{\operatorname{Im}\Sigma(\varepsilon+i\delta)}{|\varepsilon-E_0-\Sigma(\varepsilon)|^2}\,d\varepsilon = 1. \tag{6}$$

We shall now show that a sum rule similar to (6) can also be established for the products of the residues of Green's function at the poles z_k and the energy ε_k of the corresponding poles. We shall do this by applying the Cauchy residue theorem to the function $\varepsilon[G(\varepsilon) - (\varepsilon - E_0)^{-1}]$. Apart from the poles of $G(\varepsilon)$, this function has the additional pole E_0. We have

$$\frac{1}{2\pi}\int_C d\varepsilon\,\varepsilon\left(G(\varepsilon)-\frac{1}{\varepsilon-E_0}\right) = \sum_{k=0}^{\infty} z_k\frac{\varepsilon_k\Sigma(\varepsilon_k)}{\varepsilon_k-E_0} + \frac{E_0\Sigma(E_0)}{-\Sigma(E_0)}$$
$$= \sum_{k=0}^{\infty} z_k\varepsilon_k - E_0,$$

since $\varepsilon_k - E_0 - \Sigma(\varepsilon_k) = 0$ and $\Sigma(\varepsilon_k)/(\varepsilon_k - E_0) = 1$. The integral over C can readily be evaluated, and the final result is

$$\sum_{k=0}^{\infty} z_k\varepsilon_k + \frac{1}{\pi}\int_{-\infty}^{E_\infty} \frac{\varepsilon\operatorname{Im}\Sigma(\varepsilon+i\delta)}{|\varepsilon-E_0-\Sigma(\varepsilon)|^2}\,d\varepsilon = E_0. \tag{7}$$

We have thus established the properties of the poles of the Green's function, using an explicit expression for the self-energy part (3). It is possible to proceed in another way. The representation of Green's function by the sum of discrete pole terms and an integral over the continuous spectrum follows from the Lehman expansion and is unrelated to the inclusion of any particular diagrams.[5] We have shown that the analytic properties of the functions $G(\varepsilon)$ and $\Sigma(\varepsilon)$, such as the number of poles and the cut along the real half axis, are related to one another. The discrete pole terms can be extracted from the function $\Sigma(\varepsilon)$, and the remaining analytic part can be represented by a Cauchy-type integral over the boundary of the region of analyticity, i.e., the contour C. The integral over the large circle yields zero and integration over both edges of the cut yields the expression given by (3). However, in general we cannot explicitly determine the parameters a_k and E_k: they depend on which particular diagrams have been included in the self-energy part.

4. SPECTRAL DENSITY OF PHOTOELECTRONS WITH ALLOWANCE FOR MANY-ELECTRON CORRELATIONS

When many-electron correlations are taken into account, the photoionization amplitude can be represented graphically by the sequence of diagrams shown in Fig. 5. The dashed line represents the absorbed photon and the index f indicates the state of the photoelectron. The first diagram in Fig. 5 shows the photoionization amplitude without correlations. We shall suppose that the photoelectron energy is high and that its state can be adequately described by the single-particle Hartree-Fock wave function. It is therefore sufficient to take into account the effect of correlations on the hole, and this is shown in Fig. 5. Using correspondence rules

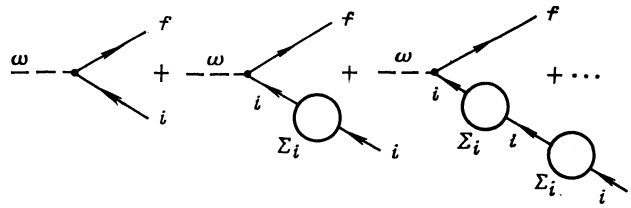

FIG. 5

and summing the diagrams, we obtain the following expression for the photoionization amplitude:

$$\langle f|D|i\rangle = \langle f|r|i\rangle\left\{1+\frac{\Sigma_i(\varepsilon)}{\varepsilon-w_i-i\delta}+\left(\frac{\Sigma_i(\varepsilon)}{\varepsilon-w_i-i\delta}\right)^2+\ldots\right\}$$
$$= \langle f|r|i\rangle\left(1-\frac{\Sigma_i(\varepsilon)}{\varepsilon-w_i-i\delta}\right)^{-1},$$

where $\varepsilon = w_f - \omega$, ω is the frequency of the absorbed photon, $\langle f|r|i\rangle$ is the photoionization matrix element, and $\Sigma_i(\varepsilon)$ is the diagonal matrix element of the self-energy part of the Green's function. The symbol $i\delta$ indicates the way the pole in the denominator is bypassed when the integral with respect to the energy of the emitted electron is evaluated in the expression for the photoionization cross section.

The photoelectron spectral density is proportional to the square of the photoionization amplitude:

$$\frac{d\sigma_i(\omega)}{dw_f} \sim |\langle f|r|i\rangle|^2\left|\left(1-\frac{\Sigma_i(\varepsilon)}{\varepsilon-w_i-i\delta}\right)^{-1}\right|^2\delta(\varepsilon-w_i).$$

Using the definition of the δ-function, we can show that

$$\left|\left(1-\frac{\Sigma_i(\varepsilon)}{\varepsilon-w_i-i\delta}\right)^{-1}\right|^2\delta(\varepsilon-w_i)$$
$$= \begin{cases} 0, & \operatorname{Im}\Sigma_i(\varepsilon)\neq 0 \\ \delta(\varepsilon-w_i-\Sigma_i(\varepsilon)), & \operatorname{Im}\Sigma_i(\varepsilon)=0 \end{cases}$$

Thus,

$$\frac{d\sigma_i(\omega)}{dw_f} = \sigma_i^0(\omega)\sum_{k=0}^{\infty} z_k\delta(\varepsilon-\varepsilon_k), \quad \varepsilon = w_f-\omega. \tag{8}$$

In the above derivation, we have used the property of the δ-function of a complex argument, and the definition of the residue of the Green function at a pole:

$$z_k = \left(1-\frac{\partial\Sigma_i(\varepsilon)}{\partial\varepsilon}\Big|_{\varepsilon_k}\right)^{-1};$$

where $\sigma_i^0(\omega)$ is the photoionization cross section of the ith shell without taking correlations into account.

Apart from the diagrams shown in Fig. 5, we must also take into account the diagrams in which the hole undergoes real decay (Fig. 6). The contribution of this sequence of diagrams to the photoionization amplitude is

$$\langle f|D|i\rangle = \langle f|r|i\rangle\left(1-\frac{\Sigma_i(\varepsilon)}{\varepsilon-w_i-i\delta}\right)^{-1}\frac{\langle ik|V|lm\rangle}{\varepsilon-w_i-i\delta}.$$

The contribution to the photoelectron spectral density is

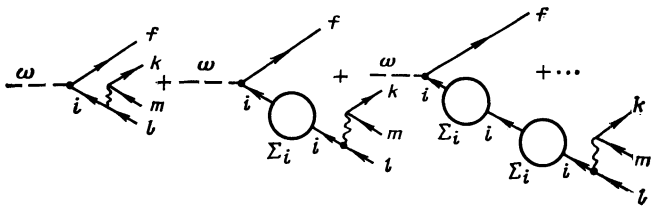

FIG. 6

$$\frac{d\sigma_i(\omega)}{dw_f} \sim |\langle f|r|i\rangle|^2 |\varepsilon - w_i - \Sigma_i(\varepsilon)|^{-2} \times \sum_k |\langle ik|V|lm\rangle|^2 \delta(\varepsilon - w_l - w_m + w_k),$$

or

$$\frac{d\sigma_i(\omega)}{dw_f} = \sigma_i^0(\omega) \frac{1}{\pi} \frac{\operatorname{Im}\Sigma_i(\varepsilon)}{|\varepsilon - w_i - \Sigma_i(\varepsilon)|^2}. \quad (9)$$

Thus, the many-particle photoelectron spectrum is found to consist of two nonoverlapping regions. In the first region, where the binding energy $\varepsilon = w_f - \omega$ is insufficient for real decay of the hole ($\operatorname{Im}\Sigma_i(\omega) = 0$), we observe discrete lines that correspond to the poles of Green's function [see (8)]. In the second region, where $\operatorname{Im}\Sigma_i(\omega) \neq 0$ and real decay is possible, we observe the poles of the continuous spectrum [see (9)].

The resultant intensity of the photoelectron spectrum is

$$\sigma_i(\omega) = \int_0^{\omega} \frac{d\sigma_i(\omega)}{dw_f} dw_f = \int_{-\omega}^{0} \frac{d\sigma_i(\omega)}{dw_f} d\varepsilon.$$

We assume that the energy of the absorbed photon is high. The lower limit in the last integral can therefore be replaced with $-\infty$, so that, using (8) and (9), we obtain

$$\sigma_i(\omega) = \int_{-\infty}^{0} d\varepsilon \sigma_i^0(\omega) \left\{ \sum_{k=0} z_k \delta(\varepsilon - \varepsilon_k) + \frac{1}{\pi} \frac{\operatorname{Im}\Sigma_i(\varepsilon)}{|\varepsilon - E_0 - \Sigma_i(\varepsilon)|^2} \right\}$$

$$= \sigma_i^0(\omega) \left\{ \sum_{k=0}^{\infty} z_k + \frac{1}{\pi} \int_{-\infty}^{E_\infty} \frac{\operatorname{Im}\Sigma_i(\varepsilon)}{|\varepsilon - E_0 - \Sigma_i(\varepsilon)|^2} d\varepsilon \right\} = \sigma_i^0(\omega), \quad (10)$$

since the expression in braces is equal to unity, according to (6).

The center of gravity of photoelectron spectrum is defined by

$$\bar{w}_f = \int_0^{\omega} w_f \frac{d\sigma_i(\omega)}{dw_f} dw_f \Big/ \int_0^{\omega} \frac{d\sigma_i(\omega)}{dw_f} dw_f.$$

Using (7) and (10), we obtain

$$\bar{w}_f = \omega + \int_{-\infty}^{0} d\varepsilon\, \varepsilon \left\{ \sum_{k=0}^{\infty} z_k \delta(\varepsilon - \varepsilon_k) + \frac{1}{\pi} \frac{\operatorname{Im}\Sigma_i(\varepsilon)}{|\varepsilon - E_0 - \Sigma_i(\varepsilon)|^2} \right\}$$

$$= \omega + \left\{ \sum_{k=0}^{\infty} z_k \varepsilon_k + \frac{1}{\pi} \int_{-\infty}^{E_\infty} d\varepsilon\, \varepsilon \frac{\operatorname{Im}\Sigma_i(\varepsilon)}{|\varepsilon - E_0 - \Sigma_i(\varepsilon)|^2} \right\} = \omega + E_0. \quad (11)$$

Thus, the center of gravity of the photoelectron spectrum corresponds to the energy of the ionized shell, $E_0 = w_i$, and the total intensity of the spectrum is equal to the intensity of the corresponding single-particle line $\sigma_i^0(\omega)$.

TABLE I. Relative intensities and energies of main lines in the photoelectron spectrum of the 3*s* shell of argon.

State	Energy, eV	Spectroscopic factor
$3s3p^6$	29.3	0.56
$3s^23p^44s$	36.7	0.03
$3s^23p^43d$	38.6	0.23
$3s^23p^44d$	41.2	0.14
$3s^23p^4\varepsilon d$	43.4	0.06

Note. The last row refers to the continuous spectrum.

The equations (6) and (7) can be used to analyze experimental photoelectron spectra. It follows from (8) and (9) that Eq. (6) is the normalization condition for the relative intensities of discrete photoelectron lines and the continuous band. These intensities can readily be measured. If we know the energy of the photoelectron lines, we can determine the left-hand side of (7) and compare it with the single-particle Hartree-Fock energy of the ionized shell. When all the discrete lines and the continuum have been correctly taken into account in the experiment, Eq. (7) should be satisfied. As an example, consider the photoelectron spectrum of the 3*s* shell of the argon atom. The relative line intensities and their energies are listed in Table I and were taken from the experimental results reported in Ref. 6. The nonrelativistic Hartree-Fock energy of the 3*s* shell, calculated by computer using the program reported in Ref. 7, is equal to 2.55 Ry. Comparison of the experimental data with calculations shows that there is good agreement:

$$\sum_k z_k \varepsilon_k = 2.56 \text{ Ry}.$$

5. CONCLUSION

We have established general relationships for the photoelectron spectrum of an atom. However, these results are valid for a wider class of spectra. For example, consider the ionizaton of an atom by a fast electron [the $(e, 2e)$ reaction]. The expressions for the ionization cross section remain unaltered when the electromagnetic vertex in the graphs of Figs. 5 and 6 is replaced by some other, for example, the inelastic scattering vertex. The main point is that the ionization process must involve sufficiently large energy transfer and the removal of a fast electron whose interaction with the ion can be adequately taken into account in the Hartree-Fock approximation.

The properties of the self-energy part and of the quasihole spectrum are not connected with the Coulomb interaction between the particles. Our results are therefore valid for other many-particle systems, for example, the nucleus. They can be used to interpret nucleon-separation spectra [the $(e, e'p)$, $(p, 2p)$, (γ, p), etc. reactions].

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