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COLLECTIVE EFFECTS, RELAXATION AND LOCALIZATION OF HOLE
LEVELS IN ATOMS, MOLECULES, SOLIDS, AND ADSORBATES X +

XX

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Collective Effects, Relaxation and Localization of
Hole Levels in Atoms, Molecules, Solids, and Adsorbates. ^{x)} +

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Abstract.

Recent progress in descriptions of photoelectron spectra is reviewed with emphasis on cases where the one-electron and quasi-particle approximations break down and the hole level becomes spread over a number of discrete lines or a continuum or both. Unifying aspects and similarities between interaction processes in atoms, molecules and solids are stressed.

1. Introduction

In recent years there has been rapid development in our understanding of the behaviour of valence and core hole levels in atoms, molecules and solids and it has become evident that one-electron pictures can break down in a vast number of different situations [1-3]. It is the purpose of the present article to outline the range of non-validity of one-electron approximations by giving a number of specific examples. An important point will be to emphasize unifying aspects and underline the similarities in both the physical phenomena and theoretical methods in the case of atoms, molecules, solids and adsorbates. Finally, the last part of this paper will deal with a particular aspect of many-electron interactions, namely excitation and deexcitation of doubly excited autoionizing resonances in N_2 , their influence on photoionization spectra and possible ways of describing the problem.

2. General features of photoelectron spectra

In a strict one-electron approximation a photoelectron spectrum consists of a single sharp line for each occupied level at a kinetic energy given by the photon energy minus the electron binding energy. The most clear direct experimental evidence for breakdown of this strict one-electron approximation is the appearance of satellite lines and Auger lines in the photoelectron spectrum. Normally Auger decay is a weak process in the sense that the initial hole is not appreciably perturbed by the Auger emission process. However, in a number of cases the emission process involves correlation between holes and electrons

in subshells partly or completely belonging to the same main shell or in different orbitals belonging to the same valence space. The interaction strength can then become so large that the properties of the initial hole levels become changed, spanning the whole range from weak satellites and moderate level shifts to complete extinction of the hole level. A convenient way of handling this problem is to treat photoionization plus Auger emission (as well as multiple ionization due to shake off) as a one-step double ionization process [2,4]. Virtual Auger processes and other relaxation processes will then give rise to structure in the initial hole level, corresponding to a variety of final ionic excited states and, in addition, there will appear an Auger spectrum at fixed kinetic energies reflecting the spectral structure of the initial interacting hole and of course also the structure of the holes in the final state. Treating the photoelectrons and the Auger electrons on the same footing ensures that one can handle cases where the time scale for the Auger decay becomes comparable to the the time scale for direct photoemission. An important such case is threshold photoemission where resonances in the absorption cross section can show up in the form of resonances in satellite and Auger spectra and where the Auger emission can influence the escaping photoelectrons and shift and distort photoelectron and Auger lines (PCI, post collision interaction; see ref. [2] for further references). In other cases the life-time of the primary hole is so short that it only acts as a virtual intermediate state [1,5] and separation of the excitation process into independent primary excitation and subsequent Auger decay again becomes meaningless.

In the cases to be discussed below in sections 3 and 4, the kinetic energy is assumed to be very high and the photoelectron spectrum can then basically be described in terms of interaction between different states of the residual ionic N-1 electron system. From this point of view, what we shall be particularly interested in are situations where the initial non-interacting hole is degenerate or nearly degenerate with and strongly interacting with a spectrum of ionic excited states, i.e. two-hole-one-electron discrete and continuum states as well as more complicated states. Particularly strong effects will occur in systems with highly polarizable valence shells, i.e. systems showing strong collective effects, in which case introduction of a hole can lead to very strong reorganization effects.

In the one-electron approximation the spectral function for the hole, describing the photoelectron spectrum, is given by a sharp line

$$A_i(E) = \delta(E - E_i^0) \quad (1)$$

where $|E_i^0|$ is the binding energy. Introducing weak life-time effects through e.g. radiative and non-radiative (Auger) decay the spectral function goes over to a Lorentzian

$$A_i(E) = \frac{1}{\pi} \frac{\Gamma_i/2}{(E - E_i^0)^2 + (\Gamma_i/2)^2} \quad (2)$$

In the general case (weak as well as strong coupling) the hole level is modified by an energy-dependent self-energy correction $\Sigma_i(E)$ leading to a spectral function for the hole level on the form

$$A_i(E) = \frac{1}{\pi} \frac{\text{Im} \Sigma_i(E)}{[E - E_i^0 - \text{Re} \Sigma_i(E)]^2 + [\text{Im} \Sigma_i(E)]^2} \quad (3)$$

The self-energy contains all information about the excited ionic states of the system as well as the coupling strength to the ionic non-interacting ground state (the single hole level in the strict one-electron approximation), and by studying the solutions to the Dyson equation

$$E - \epsilon_i^0 = \text{Re} \Sigma_i(\epsilon) \quad (4)$$

one obtains information about the discrete structure in the spectrum. In the neighbourhood of a spectral peak the spectral function takes the form

$$A_i(\epsilon) = \frac{Z(\epsilon)}{\pi} \frac{\Gamma_k/2}{(\epsilon - \epsilon_k)^2 + (\Gamma_k/2)^2} \quad (5)$$

$$Z(\epsilon) = [1 - \partial \text{Re} \Sigma_i(\epsilon) / \partial \epsilon]^{-1} \quad (6)$$

$$\Gamma_k/2 = Z(\epsilon) \text{Im} \Sigma_i(\epsilon) \quad (7)$$

which connects back to Eq. (2) and shows how to extract line parameters knowing the self-energy. However, in the really interesting cases, the line parameters become strongly energy-dependent and even meaningless and one then has to calculate the spectrum directly from Eq. (3), which directly describes both the discrete and the continuous features of the hole spectrum.

3. Dynamical relaxation and localization of hole levels

Spectacular many-body effects may occur when a hole is introduced in a subshell belonging to an open main shell (i.e. one or several subshells are partially or completely empty) in an atom or molecule or in the valence band of a narrow-band metal. The hole level is then poorly described by the atomic, molecular or band orbital picture and must be represented in terms of a distribution of symmetry orbitals, i.e. in terms of a more or less localized wave packet that moves through the system in the form of a quasi-hole, dragging along its screening cloud. This is of course a well known concept in the theory of solids but it is actually equally, if not more, important in many atoms and molecules. The wave packet distortion of the hole orbital can couple to induced distortions of the valence charge distribution and considerably reduce the energy of the hole by building up a localized screening charge that follows the moving hole. We are thus dealing with a dressed hole, a quasi-hole. The notable thing is that the relaxation shift associated with the dynamical localization of the hole often is considerably larger than the usual static "monopole" relaxation shift obtained e.g. from a ASCF calculation by forcing the hole to remain in a symmetry orbital.

Let us now consider a few specific examples [1] such as (i) the 4p hole levels in Pd to Ce, (ii) inner and outer valence hole and core hole levels in molecular nitrogen, N_2 , and (iii) a hole in the 3d-valence band in Ni metal.

(i) Experimentally, both of the 4p X-ray photoelectron lines disappear as one proceeds from $_{46}\text{Pd}$ through $_{48}\text{Cd}$ to $_{50}\text{Sn}$ and $_{52}\text{Te}$ [6]. In $_{53}\text{I}$ and $_{54}\text{Xe}$ [7] a discrete peak reappears and from $_{55}\text{Cs}$, $_{56}\text{Ba}$ [7] and onwards [6] this peak may be regarded as a strongly distorted and shifted 4p $^2P_{3/2}$ hole level. However, the main $^2P_{1/2}$ hole level remains absent and does not reappear until the 4f-shell is filled at the end of the rare earth series. The explanation [1,5] is that the 4p hole levels are degenerate with a continuum of $4d^2\epsilon f$ excitations (a bar under an orbital index indicates a hole) and coupled to this continuum through a giant Coster-Kronig fluctuation and decay process [1,5] $4p \nrightarrow 4d^2\epsilon f$ as shown in Fig. 1a. The final state involves a 4f-like band of levels which results in a very large coupling strength, of the order of the intra-shell Coulomb interaction. The combined effect of continuum density of f-levels and the coupling strength is given by the imaginary part of the hole self-energy $\text{Im } \Sigma_{4p}(E)$. For $_{50}\text{Sn}$ and $_{52}\text{Te}$ $\text{Im } \Sigma_{4p}(E)$ is rather flat and broad and the dispersion of $\text{Re } \Sigma_{4p}(E)$, which is obtained from the imaginary part through a Kramers-Kronig relation, is too small to split off a state from the continuum. Instead there is no quasi-hole solutions at all and the resulting spectral function (Fig.1b) just becomes a broad continuum distribution ($\sim 20\text{-}30$ eV FWHM). This is then a text-book example of complete breakdown of the one-electron picture as well as the quasi-particle picture for a hole level. Proceeding towards higher atomic number Z, the f-electron level density acquires a narrow-band character, in particular on the low-energy side, and the dispersion of $\text{Re } \Sigma_{4p}(E)$ is now so strong that a $^2P_{3/2}$ level

becomes split off from the band (Fig. 1c) and appears as a narrow line in the spectral function. This solution of Eq. (4) represents a stable quasi-hole in the form of a distorted 4p hole together with its screening charge. In $_{50}\text{Sn}$ and $_{52}\text{Te}$ the screening charge is built up from continuum f-states so that the 4p hole very rapidly can dissipate its energy. The hole therefore exists only for a very short time, there are no quasi-hole solutions and the spectral function takes the form of a broad quasi-resonant continuum distribution. Expressed in classical terms one might say that in Xe the 4d-shell responds in an elastic manner to the perturbation by the 4p-hole while in Sn and Te it responds more like a viscous fluid.

(ii) In the N_2 molecule there is direct evidence for the importance of many-body effects in the form of prominent satellites in photoelectron spectra. Indirect evidence, through comparison with theory, is that the restricted HF scheme predicts wrong ordering for the $3\sigma_{-g}$ and $1\Pi_{-u}$ hole levels and there are large relaxation shifts not accounted for by the HF ΔSCF method for the valence levels $3\sigma_{-g}$ (~ 2 eV), $2\sigma_{-u}$ (~ 2.5 eV), $2\sigma_{-g}$ (~ 3 eV) and for the core levels $1\sigma_{-g}$, $1\sigma_{-u}$ (~ 10 eV). In order to account for these differences one has to describe the holes as mixtures of gerade and ungerade molecular symmetry orbitals which, in a snapshot picture, breaks the molecular symmetry and introduces a localized perturbation [1,8,9]. This perturbation induces a corresponding localized perturbation of the valence charge and can lead to a large additional relaxation shift. Expanded in a MO picture, the hole jumps between gerade and ungerade levels and is coupled to corresponding fluctuations of the

valence electrons, as shown in Fig. 1d. In the extreme case of $1\sigma_g$, $1\sigma_u$ core holes the effect is to create a $1s$ hole localized on either nucleus coupled to a corresponding distortion of the $\sigma-\pi$ valence charge [1,10,11]. Since the time for this aggregate to hop between the nuclei is much longer than the life-time due to e.g. Auger decay, for practical purposes the excitation breaks the molecular symmetry and must be regarded as localized. If one could increase the $\sigma_g-\sigma_u$ splitting at will, one could then make the localized hole and its screening cloud start to oscillate between the nuclei. As the hopping time becomes shorter than the life-time the quasi-hole can oscillate several times before decaying and must therefore represent an eigenstate of the molecular symmetry. However, this does not mean that that a description in terms of a single molecular symmetry orbital is valid because the hole must still be represented as a gerade-ungerade mixture of levels, as is very clear in the case of $2\sigma_g$, $2\sigma_u$ and $3\sigma_g$ hole levels in N_2 .

Even if there are strong many-electron effects, as long as most of the spectral strength goes into a particular spectral line the quasi-particle picture is valid and the hole can be associated with a well-defined molecular excitation. However, there is now strong evidence that in many molecules holes in the inner valence region become split up on a large number of fairly weak spectral lines. This is analogous to the case of the $4p$ hole levels in Sn and Te becoming spread over a continuum and represents a complete breakdown of the quasi-particle picture. The $2\sigma_g$ level in N_2 does show signs of multi-level structure but much more spectacular effects are found e.g. in N_2O_4 and HCN [3].

(iii) We can now consider extending the above picture to a long chain of atoms so that we approach a band picture (Fig. 1e). If the hole is created in a narrow band the corresponding localized wavepacket will move slowly enough that the screening cloud due to the response of the valence electron can follow adiabatically. If the Auger width is considerably less than the bandwidth, the quasi-hole will then have time to move far enough to experience the periodicity of the potential. Well-resolved photoelectron peaks will therefore represent good quasi-hole band states which, however, does not mean that a standard one-electron band structure calculation is valid [12].

The hole can also be introduced in the valence band and will then be subject to intra-valence shell fluctuation and decay processes, as shown in Fig. 1f. In a broad band the effect will only be to give the quasi-particle an effective mass and a lifetime (see e.g. Ref. [13]). However, since the fluctuation process takes place within a single band, it is analogous to the giant Coster-Kronig fluctuation and decay process in the atomic case. The coupling strength is then of the order of the intraband Coulomb interaction and if the bandwidth is small enough, discrete structure could be split off from the band, as schematically shown in Fig. 1g. Physically, this means that the valence hole moves so slowly that there is charge relaxation around it, leading to a relaxation shift of the band states and to the appearance of shake up satellite structure (Fig. 1g). There are strong indications that the above picture of dynamic localization and relaxation has some relevance for describing photoelectron spectra for the 3d-valence band in metallic

Ni and might account for the observed band narrowing and the 6 eV satellite structure and also for the resonance of the satellite versus the main 3d-band in the region of the 3p-ionization threshold [14-20] (for an analogous case of resonant satellites in atomic Ba, see Ref. [2]).

4. Satellite spectra and charge transfer processes

Creation of an inner valence or core hole in an atom, molecule or solid may sometimes cause part of the outer valence charge distribution to collapse and reorganize in a drastic manner. The reason is that under the influence of the increased effective nuclear charge a previously empty level can move down to the vicinity of the filled valence levels or even below the Fermi level, in which case it can become filled by a transition from the valence levels. In a time-resolved classical type of picture the valence charge can then oscillate in response to creation of a hole and in an energy-resolved photoelectron spectrum the spectral strength of the hole will become split up on several lines representing the possibilities that the pulled down level can be filled or remain empty. One can also say that certain shake up satellites move down to the region of and below the unperturbed main line and the subsequent configuration interaction can give rise to a complicated spectrum where some lines may be referred to as shake down lines because they occur at the low binding energy side of the main line.

A very interesting example is found in atomic Ba [21] where a 5p hole causes an empty 5d-level to move below the filled 6s-level, resulting in an open shell type of final ionic state. A hole in the $5p\ ^2P_{3/2}$

level can then induce a 6s-5d transition and one might talk about intra-atomic inter-shell charge transfer. The atomic orbital picture for the $5p^2 P_{3/2}$ level breaks down completely and the spectrum consists of a number of lines corresponding to the normal modes of the coupled $5p, 5d, 6s$ system subject to the atomic symmetry [1,2,22].

In proper transition metal (TM) and rare-earth (RE) charge transfer complexes the presence of very strong satellite lines has been known for a long time [23-26]. As an example, a 3d-hole in the lanthanum compounds LaF_3 , $LaCl_3$ and $LaBr_3$ [24-26] will cause an empty 4f-orbital localized on the La ion to move down to the region of the filled halogen valence p-levels. In response to the sudden creation of a 3d-core hole one can then imagine the ligand p-charge to oscillate along the metal-ligand bonds and in an energy-resolved photoelectron spectrum one would typically observe two peaks in the 3d-region, a main peak corresponding to an eigenstate where the screening charge remains on the ligands and the 4f La-level is empty and a satellite where the 4f-level is filled. The satellite can appear both at higher (LaF_3) and lower ($LaBr_3$) binding energy than the main line, in which cases it will be weaker than the main line, and there is an intermediate situation where the two levels have about the same strength and the distinction between main line and satellite becomes meaningless ($LaCl_3$). Actually it may be more appropriate to classify also $LaBr_3$ in this way and in addition e.g. La_2O_3 falls into the same class. The possibility of having charge transfer satellites on the low binding energy side of the main line was discussed already in Ref. [26].

One may now ask what happens to the 3d-core level in metallic La. The answer seems to be that again an empty 4f-level becomes pulled down into the Fermi sea of 6s-5d electrons but the coupling to the valence band is very weak. As a result, the main 3d-lines represent excited ionic states where the 4f-level remains empty, and reaching the lowest energy level with the screening charge in a 4f-level becomes quite improbable. However, in experimental photoelectron spectra from Ref. [27] there is a distinct bump on the low binding energy side of the main $3d_{5/2}$ line in La and Ce (probably also for the $3d_{3/2}$ level but this is obscured by high energy satellite structure on the $3d_{5/2}$ line). To my knowledge this is the first clear experimental evidence for satellite structure on the low binding energy side of a core line in a metal. More recently, the $3d_{5/2}$ core level has been studied experimentally in a systematic manner in Ba to Nd metal [28], and it has been convincingly demonstrated that the 4f-level moves down into the Fermi sea between Ba and La but that the main $3d_{5/2}$ line corresponds to the case of the 4f-level remaining empty. This is in sharp contrast to the 3d-metals where the main core lines also represent the lowest level.

A closely related situation occurs in photoionization of molecules adsorbed on transition metal surfaces as well as in the corresponding transition metal-molecule complexes. As an example, 1s-ionization of CO adsorbed on metallic Ni may cause a CO 2π level to move down into the 3d-valence region below the Fermi level of the metal and hybridize with the metal 3d-band, and as a result, screening charge may oscillate between the substrate and the adsorbate. The theoretical hole spectrum again contains several components with the possibility of having charge transfer satellites on the low binding energy side of the main line, and such phenomena also seem to have been observed experimentally [29-32].

5. Autoionizing resonances in molecular photoionization spectra

In recent experimental investigations of photoionization spectra for molecular nitrogen N_2 [33] there appears a peak around 23 eV photon energy in the $3\sigma_g$ partial cross section (also visible in the absorption cross section) which cannot, it seems, be described in terms of single excitations. MSX α calculations [34-35] qualitatively account for the shape resonance in the $3\sigma_g \rightarrow \sigma_u$ channel at around 26 eV and HF-type of calculations [36], taking into account the proper symmetry of the excitation, even give reasonable quantitative agreement with experiment. However, both approaches fail to account for the 23 eV peak, and since there is no discrete single electron excitation in this energy range one is led to consider the possibility of double excitations. In high resolution photoabsorption measurements [37] one observes fine structure superimposed on the 23 eV peak converging to the $C^2\Sigma_u$ ionization

threshold, which corresponds to a final ionic excited state $3\sigma_g^{-1}(1\pi_u 1\pi_g)^2 \Sigma_u^2$ and appears as a prominent satellite to the main $2\sigma_u$ outer valence level in a photoelectron spectrum. The fine structure has been identified as due to vibrationally split Rydberg-like excitations converging to the $C \Sigma_u^2$ level and therefore representing double excitations [37]. We suggest (see also Ref. [38]) that also the 23 eV peak is associated with an autoionizing resonance in the form of a very compact non-Rydberg-like double excitation having the configuration $3\sigma_g^{-1}\pi_u^{-1}\pi_g^2$ and autoionizing into the $3\sigma_g \epsilon \sigma_u$ channel (Fig. 2a,b). Since all of the orbitals in this double excitation belong to the valence space and the shape resonance in the $3\sigma_g \epsilon \sigma_u$ channel tends to localize in the same region of space as the valence electrons, the coupling strength could be large and might account for the large oscillator strength and width of the experimental 23 eV peak.

The excitation and decay mechanism for such a resonance is outlined in diagrammatic form in Fig. 2c-f in the case of a single discrete resonance interacting with a single continuum channel. The effective ionization amplitude $D_\epsilon(\omega)$ in the $3\sigma_g \epsilon \sigma_u$ channel (Fig. 2c) can be broken up in a non-resonant part $D_\epsilon^0(\omega)$ (Fig. 2d) describing direct emission, and a resonant part describing excitation and decay of the doubly excited discrete level (Fig. 2e,f). The resonant part contains an effective excitation amplitude $P_d(\omega)$ for reaching the doubly excited configuration (Fig. 2g-i) and an effective interaction $V_{d\epsilon}$ for coupling to the $3\sigma_g \epsilon \sigma_u$ single ionization channel. Also, since the system can jump back and forth, figuratively speaking, between the discrete level

and the continuum, there appears an effective interaction $S_d(\omega)$ within the discrete level due to coupling to the continuum. Summing the infinite series indicated in Fig. 2e,f leads to a dynamic shift of the discrete level and the ionization amplitude can be written as

$$D_\xi(\omega) = D_\xi^0(\omega) - \frac{P_d(\omega) V_{d\varepsilon}}{\omega_d - \omega - S_d(\omega)} \quad (8)$$

With the differential cross section, describing the intensity variation of the $3\sigma_g$ photoelectron line, given by

$$\frac{d\sigma(\omega)}{d\varepsilon} = 4\pi^2 \alpha a_0^2 \omega |D_\xi(\omega)|^2 \delta(\varepsilon - E_{3\sigma_g} - \omega) \quad (9)$$

(α is the fine structure constant and a_0 the Bohr radius) one obtains the Breit-Wigner-Fano line shape formula

$$\frac{d\sigma(\omega)}{d\varepsilon} = \frac{d\sigma^0(\omega)}{d\varepsilon} \frac{(\zeta + Q)^2}{\zeta^2 + 1} \quad (10)$$

where

$$\frac{d\sigma^0(\omega)}{d\varepsilon} = 4\pi^2 \alpha a_0^2 \omega |D_\xi^0(\omega)|^2 \delta(\varepsilon - E_{3\sigma_g} - \omega) \quad (11)$$

$$\zeta = (\omega - \omega_d + \Delta(\omega)) / \frac{1}{2} \Gamma(\omega) \quad (12)$$

$$Q = - \operatorname{Re} P_d(\omega) / \operatorname{Im} P_d(\omega) \quad (13)$$

$$\Delta(\omega) = \operatorname{Re} S_d(\omega) \quad (14)$$

$$\frac{1}{2} \Gamma(\omega) = \operatorname{Im} S_d(\omega) \quad (15)$$

$$= \pi \int d\varepsilon |V_{d\varepsilon}|^2 \delta(\varepsilon - E_{3\sigma_g} - \omega)$$

In order to calculate the line shape parameters one must evaluate the expressions for the effective coupling matrix elements $P_d(\omega)$, V_{dc} and $S_d(\omega)$ and this raises the question of basis states. The basic idea of the present investigation is to use basis functions similar to what is obtained with the MSX α method, however avoiding if possible the muffin-tin approximation. In other words, we wish to start from a local-density approximation that gives a fairly good representation of the ground state potential, and all effects of reorganization in response to the excitation will then have to be accounted for by infinite order perturbation theory, leading to renormalized, effective coupling matrix elements of physical significance. One has then to work on the level of the random phase approximation with exchange (RPAE) and beyond. In this way the effective direct ionization amplitude $D_e^0(\omega)$ will give results quite similar to Ref. [36], coupling the electron-hole excitation to the proper molecular symmetry.

Numerical calculations are in progress but results are not yet available. In the present investigation we intend to work explicitly with molecular continuum functions [38]. The MSX α method is very convenient for generating molecular continuum functions but the muffin-tin approximation may represent too strong a distortion of the true molecular potential for accurate descriptions of resonant states, although in principle one could correct for this in perturbation theory. Removing the muffin-tin condition brings us back to the full complexity of molecular calculations, matching multi-centre molecular wave functions at small radii to one-centre continuum wave functions at

large radii. We are therefore presently investigating the usefulness of one-centre expansions at all distances, constructing a two-centre molecular potential from overlapping atomic local-density potentials and reexpanding the potential with respect to the centre-of-mass of the molecule.

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Figure captions

- Fig. 1. Fluctuation and decay processes involving hole levels in atoms (a), molecules (d), and solids (e,f). Schematic pictures of the associated variation in the hole self-energy $\Sigma_1(E)$, solutions of the Dyson Eq. (4), and the spectral function $A_1(E)$ (b,c,g).
- Fig. 2. Diagrammatic expansion of the interaction of the doubly excited discrete $3\sigma_{-g} 1\pi_{-u} 1\pi_g^2$ configuration with the continuum $3\sigma_{-g} \epsilon\sigma_u$ direct photoionization channel (see text).

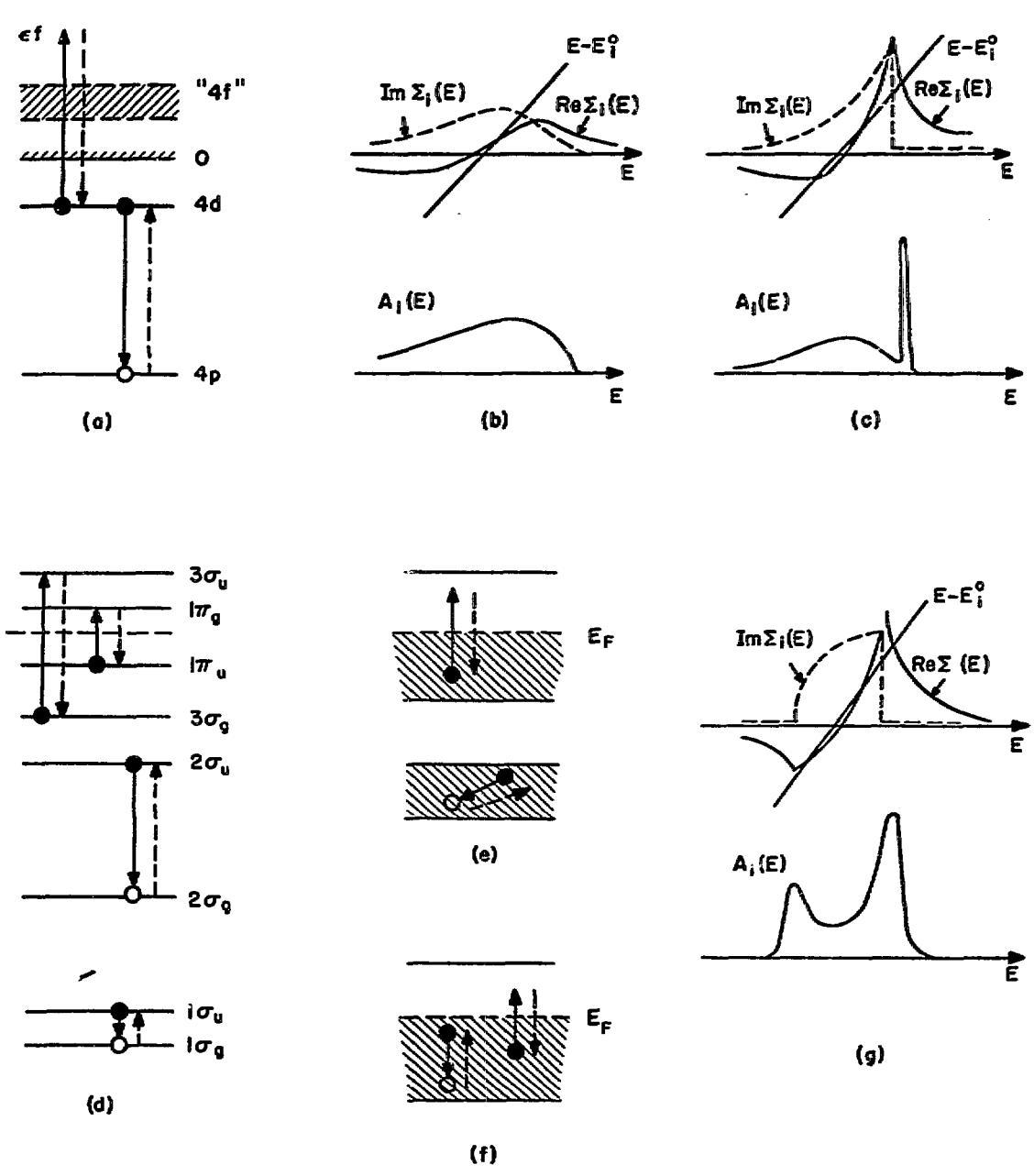


Figure 1

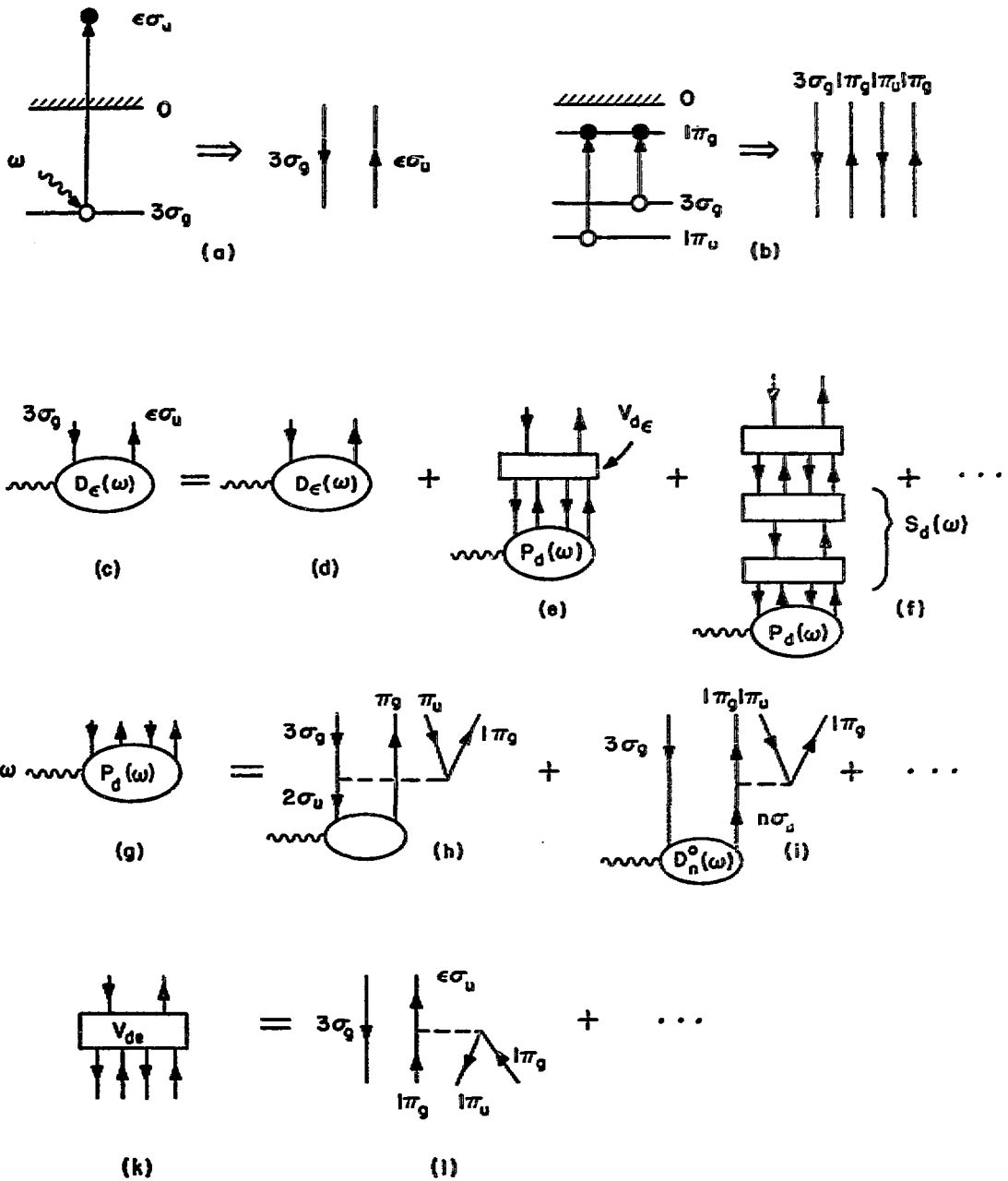


Figure 2