

Some theoretical studies on concurrent events in photoelectron spectroscopy

M S GOPINATHAN and B J CHERAYIL

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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Abstract. Concurrent events in photoelectron spectroscopy such as photoionisation, shake-up and shake-off transitions are studied using atomic wavefunctions recently developed by one of the authors and the concept of the Slater transition state. Various transition energies and intensities are calculated to test the efficiency of the wavefunctions and the applicability of the transition state method to these processes. It is concluded that the method is reliable enough to be useful in the assignment of these transitions in the experimental spectrum.

Keywords. Ionisation potential; shake-up and shake-off processes; HFG wavefunctions; Slater transition state; photoelectron spectroscopy.

1. Introduction

Photoelectron spectroscopy (Siegbahn *et al* 1969; Baker and Betteridge 1972; Carlson 1975) has now developed into a powerful tool for selectively probing the energy levels in atoms and molecules. In this branch of spectroscopy one measures the kinetic energy of electrons expelled by incident x-ray or UV photons of known energy and thus obtains the ionisation energy of the bound electrons. But concurrent with this photoionisation process, other events also take place. The sudden creation of a one-electron vacancy in an atom or molecule may render the system sufficiently disturbed as to either excite a valence electron to a higher energy level or to expel it from the system altogether. The former process is known as shake-up and the latter as shake-off. These transitions appear in the photoelectron spectra as weak satellites of the main ionisation peak.

The study of the shake-up and shake-off transitions can lead to important information about molecular properties. For instance, a definite relationship has been established between shake-up satellites and paramagnetism in transition metal compounds (Matienzo *et al* 1973; Vernon *et al* 1976). The shake-up energies have also been found (Matienzo *et al* 1973) to correlate with the nephelauxetic series of the ligands. Furthermore, the high degree of precision with which these transition energies and intensities can be measured make them especially useful in testing theoretical models of these processes.

The purpose of the present paper is two-fold: (i) To apply the Slater transition state (STS) method (Slater 1974) to describe ionisation, shake-up and shake-off processes. Though STS has been employed successfully to describe ionisation (Schwarz 1975; Gopinathan 1979), it does not seem to have been widely used before, for the latter two

processes (Sen 1979). (ii) To test the efficiency of the atomic potential and wavefunctions developed earlier (Gopinathan 1977). This method, designated HFG, has been used previously for eigenvalues of the one-electron equations (Gopinathan 1977; Sen 1980), total energies (Tseng *et al* 1980; Tseng and Whitehead 1981), spin density distribution (Gopinathan 1977; Tseng and Whitehead 1981), Sternheimer antishielding factors (Sen and Weiss 1979) and dipole polarisabilities of ionic crystals (Maessen and Schmidt 1981). In all these cases the HFG wavefunctions have been found to be more accurate than the traditionally popular Hartree-Fock-Slater (HFS) wavefunctions (Herman and Skillman 1963). We propose here to use the HFG wavefunctions to describe events in photoelectron spectroscopy.

The present paper is organised as follows. In § 2.1 a brief description of the STS method is given and in 2.2 equations are derived for ionisation shake-up and shake-off energies in this method. Section 2.3 describes the relevant aspects of the HFG wavefunctions. Finally § 3 presents the results and conclusions.

2. Theory

2.1 The Slater transition state

Ionisation potential for an atom or a molecule may be calculated by several methods. In the Δ SCF method the ionisation potential is given by the difference between the total SCF energies of the ion and the atom. A good approximate estimate of the ionisation potential is alternatively given by Koopmans theorem (Koopmans 1933), which however ignores relaxation effects. Slater (1970) originally proposed a transition state method to calculate the relaxed ionisation potentials in the X_α method. This method has since been generalised (Goscinski *et al* 1973) to other SCF theories as well. However we are concerned here only with the X_α methods and the highlights of an alternate derivation of the STS method in the X_α theory given earlier (Gopinathan 1979) are reproduced below for convenience of later discussion. The reader is referred to the original paper for details and for a discussion of the extent of relaxation involved in the STS method. The total energy of an atom in the X_α method can be written as

$$E = \sum_i n_i \langle i | i \rangle + (1/2) \sum_i \sum_j n_i n_j \langle i | | j \rangle + c a_\uparrow \langle \rho_\uparrow^{4/3}(1) \rangle + c a_\downarrow \langle \rho_\downarrow^{4/3}(1) \rangle. \quad (1)$$

Here n_k is the occupancy of the spin orbital u_k which is a solution of the one-electron Schrödinger equation,

$$\{f_1 + \sum_j \langle u_j^*(2) u_j(2) g_{12} \rangle + (4/3) c a_\uparrow \rho_\uparrow^{1/3}(1)\} u_{k\uparrow}(1) = \epsilon_k u_{k\uparrow}(1) \quad (2)$$

with

$$f_1 = \nabla_1^2 - 2Z/r_1; \quad g_{12} = 1/|r_1 - r_2| \text{ and } c = - (9/2) (3/4\pi)^{1/3},$$

and α_{\uparrow} and α_{\downarrow} are the parameters of the X_{α} theory (Schwarz 1972, 1974; Gopinathan *et al* 1976; Tseng and Whitehead 1981). The integrals in (1) and (2) are defined as

$$\begin{aligned}\langle i | i \rangle &= \int u_i^* (1) f_1 u_i (1) d\tau_1, \\ \langle i \| j \rangle &= \int u_i^* (1) u_i (1) g_{12} u_j^* (2) u_j (2) d\tau_1 d\tau_2, \\ \langle X(n) \rangle &= \int X(n) d\tau_n.\end{aligned}\quad (3)$$

From (2) the X_{α} eigenvalue is

$$\epsilon_k = \langle k | k \rangle + \sum_j n_j \langle k \| j \rangle + (4/3) c \alpha_{\uparrow} \langle u_k^* (1) u_k (1) \rho_{\uparrow}^{1/3} (1) \rangle. \quad (4)$$

The unrelaxed ionisation potential for the k th orbital, I_k^{ur} may be calculated by setting $n_k = 1$ for the neutral state and $n_k = 0$ for the ion in (1) and taking the difference keeping the u 's the same as in the neutral state. This leads to, after some approximations,

$$\begin{aligned}I_k^{ur} &= - \langle k | k \rangle - \sum_{j \neq k} n_j \langle k \| j \rangle - (1/2) \langle k \| k \rangle \\ &\quad - (4/3) c \alpha_{\uparrow} \langle u_k^* (1) \rho_{\uparrow}^{1/3} (1) \rangle.\end{aligned}\quad (5)$$

Comparison of (4) and (5) shows that

$$I_k^{ur} = - \epsilon_k + (1/2) \langle k \| k \rangle. \quad (6)$$

Thus the X_{α} eigenvalue differs from the Koopmans' ionisation potential by $(1/2) \langle k \| k \rangle$, the self-interaction term. This discrepancy can be removed by using a state of fractional occupation number (Slater transition state) which is a state intermediate between the neutral and ionised states. Thus for the state $n_k = \frac{1}{2}$, the eigenvalue becomes

$$\begin{aligned}\epsilon_k (n_k = \frac{1}{2}) &= \langle k | k \rangle + \sum_{j \neq k} n_j \langle k \| j \rangle + \frac{1}{2} \langle k \| k \rangle \\ &\quad + (4/3) c \alpha_{\uparrow} \langle u_k^* (1) \rho_{\uparrow}^{1/3} (1) \rangle.\end{aligned}\quad (7)$$

This is identical in magnitude to the I_k^{ur} defined by (5). Therefore

$$I_k^{ur} = - \epsilon_k (n_k = 1/2). \quad (8)$$

Since a state intermediate between the neutral and ionised states is employed, some amount of relaxation is taken care of by (8) in actual computations (Gopinathan 1979). The ionisation potentials calculated by this method have been found to be more accurate than those calculated by the other methods mentioned above (Schwarz 1975; Gopinathan 1979). However no calculations of shake-up or shake-off energies using the STS method appear to have been reported. Presently we try to determine the utility of the STS method in the study of these processes with HFG wavefunctions.

2.2 The transition state for shake-up and shake-off processes

In a shake-up transition, the initial and final states of the atom may be described by specifying the occupancies n_i of the various spin orbitals involved in photoionisation. If primary ionisation takes place from the k th orbital and if shake-up occurs between the l th and m th orbitals, we have for the initial state (I): $n_k = 1$, $n_l = 1$ and $n_m = 0$ and for the final state (F): $n_k = 0$, $n_l = 0$ and $n_m = 1$. The difference in the total energies of these two states gives the shake-up transition energy (ΔE^{su}) and is easily shown, using (1), to be

$$\begin{aligned} \Delta E^{\text{su}} &= E_F - E_I \\ &= \langle m | m \rangle - \langle l | l \rangle + \sum_{j \neq k, l, m} n_j \langle m || j \rangle - \sum_{j \neq k, l, m} n_j \langle l || j \rangle \\ &+ (1/2) \langle m || m \rangle - (1/2) \langle l || l \rangle \\ &+ (4/3) ca_{\uparrow} \langle \rho_{\uparrow}^{1/3} (1) \{ u_m^2 (1) - u_l^2 (1) \} \rangle. \end{aligned} \quad (9)$$

If we now choose a transition state t defined by occupancies $n_k = 1/2$, $n_l = 1/2$ and $n_m = 1/2$, the expressions for the transition state eigenvalues ϵ_l^t and ϵ_m^t are from (4),

$$\begin{aligned} \epsilon_l^t &= \langle l | l \rangle + \sum_{j \neq k, l, m} n_j \langle l || j \rangle + (1/2) \langle l || l \rangle + (1/2) \langle l || m \rangle \\ &+ (4/3) ca_{\uparrow} \langle u_l^2 (1) \rho_{\uparrow}^{1/3} (1) \rangle, \end{aligned} \quad (10)$$

$$\begin{aligned} \text{and } \epsilon_m^t &= \langle m | m \rangle + \sum_{j \neq k, l, m} n_j \langle m || j \rangle + (1/2) \langle m || m \rangle + (1/2) \langle m || l \rangle \\ &+ (4/3) ca_{\uparrow} \langle u_m^2 (1) \rho_{\uparrow}^{1/3} (1) \rangle. \end{aligned} \quad (11)$$

It readily follows by comparing (9), (10) and (11) that

$$E^{\text{su}} = \epsilon_m^t - \epsilon_l^t. \quad (12)$$

Thus the shake-up energy is given by the difference in the transition state eigenvalues of the two levels involved in the shake-up process.

Following similar arguments the energy for the shake-off process, ΔE^{so} , is easily shown to be

$$\Delta E^{\text{so}} = -\epsilon_i^f, \quad (13)$$

where we have taken the occupancies for the initial state as $n_k = 0$ and $n_i = 1$, for the final state as $n_k = 0$ and $n_i = 0$ and for the transition state as $n_k = 0$ and $n_i = \frac{1}{2}$. Thus the shake-off energy is simply the negative of the transition state eigenvalue of the level from which the shake-off electron is ejected.

The shake-up and shake-off transition probabilities have been treated successfully using the sudden approximation (Manne and Aberg 1970; Gelius 1974; Watson and Perlman 1975). This approximation is based on the assumption that the time scale involved in the photoemission is extremely small such that in the wavefunction $\phi_i(N-1)$ for the $(N-1)$ -electron system immediately after photoemission, all the $(N-1)$ orbitals except that of the missing i th electron are frozen in the forms they had in the initial N -electron state $\Psi_0(N)$. Physically this means that the photoemission is so rapid that the remaining electrons have no time to readjust themselves to the new potential before shake-up or shake-off occurs. The change in the Hamiltonian due to ionisation is instantaneous so that we can approximate the initial state of the shake-up and shake-off processes by an antisymmetrised product of the orbitals of the neutral atom. $\phi_i(N-1)$ is not an eigenfunction of the actual $(N-1)$ -electron system, but it may be expanded in a complete set of such eigenfunctions $\chi_n(N-1)$ as,

$$\Phi_i(N-1) = \sum_n \{ \langle \Phi_i(N-1) | \chi_n(N-1) \rangle \chi_n(N-1) \}, \quad (14)$$

where $\langle \Phi_i | \chi_n \rangle$ is an overlap integral. The probability of a monopole transition to the n th state of the ion after photoemission is then simply

$$P_{\text{in}} \propto | \langle \Phi_i | \chi_n \rangle |^2. \quad (15)$$

The intensity of a shake-up transition can be calculated therefore from the overlap integral between the concerned atomic orbitals in the neutral and ionised systems. Results of such calculations are given in § 3.

2.3 HFG wavefunctions

Wavefunctions used in the present study have been obtained using the HFG potential referred to in § 1. Here we recall the highlights of the method (see Gopinathan 1977 for details). In this method one solves the one-electron Schrödinger equation

$$\{ -\nabla^2 - 2Z/r + V^c(r) + V_i^{\text{HFG}}(r) \} u_i(r) = \epsilon_i u_i(r). \quad (16)$$

Here the coulomb potential is given by

$$V^c(r) = \int \rho(r') 1/|r - r'| dr' \quad (17)$$

and the exchange correlation potential $V_i^{\text{HFG}}(r)$ is separated into a self-interaction part $V_i^s(r)$ and a pure exchange part $V_i^{\text{ex}}(r)$,

$$V_i^{\text{HFG}}(r) = V_i^s(r) + V_i^{\text{ex}}(r), \quad (18)$$

with
$$V_i^s(r) = -n_i \int u_i^*(r) u_i(r') (1/|r - r'|) dr', \quad (19)$$

and
$$V_i^{\text{ex}}(r) = - (9/2) (3/4 \pi) \{2\rho_{i'}(r) \rho^{-2/3}(r) - (2/3) \rho^{-5/3}(r)$$

$$\sum_i n_i u_i^*(r) u_i(r) \rho_{i'}(r)\} \quad (20)$$

Here
$$\rho(r) = \sum_i n_i u_i^*(r) u_i(r),$$

$$\rho_{i'}(r) = \rho(r) - n_i u_i^*(r) u_i(r),$$

and a is the exchange parameter occurring in the X_a theory. However it has been shown earlier (Gopinathan *et al* 1976) that the parametric nature of the exchange potential can be dispensed with by a consideration of some properties of the Fermi hole which leads to:

$$a = (8/27) (4\pi^2/3)^{1/3} (1/n + 1/2) / (1/n + 1/3)^{2/3}, \quad (21)$$

where n is the number of electrons of a given spin in an atom. The theoretical exchange potential defined by (20) and (21) has been used in the present study as it has been found to be superior (Gopinathan and Rao 1980) to potentials employing empirical values of a . After the completion of this work we have come across the attempt by Tseng and Whitehead (1981) to reparametrise the HFG potential.

3. Results and discussion

A few rare gas atoms have been chosen for the present study as some experimental and previous theoretical studies are available for comparison.

The photoionisation energies of various levels in the rare gas atoms neon, argon, krypton and xenon calculated by the HFG-STS method are compared with the experimental values in table 1. While the agreement between the experimental and calculated values is fairly satisfactory, the large errors in some instances suggest that the method may not be entirely reliable. Relativistic effects are neglected in the present study. These may appreciably change the predicted values especially for heavier atoms. It may also be pointed out here that the Koopmans theorem does not hold (Gopinathan 1979) for the eigenvalues of the X_a methods, HFS or HFG, and hence a

Table 1. Energies of photoionisation peaks of rare gas atoms.

Atom	Ionising level	ΔE in eV	
		Exptl. ^a	Present work
Ne	1s	870.2	863.6
Ar	2s	326.3	349.5
	2p	248.5	292.5
Kr	3p	214.4	235.8
	3d	93.7	126.8
Xe	3d	676.4	751.7
	4d	67.5	90.1

^aFrom Spears *et al* (1974).

Table 2. Shake-up transition energies in rare gas atoms.

Atom	Ionising level	Transition	ΔE in eV		HF ^a
			Exptl. ^a	Present work	
Ne	1s	2p → 3p	37.3	44.9	37.6
			40.7		37.6
	1s	2p → 4p	42.3	48.5	
			46.4		
1s	2p → 5p	44.2	50.1		
1s	2s → 3s	60.0	65.6		
Ar	2s	3p → 4p	23.4	26.9	22.2
			23.7		22.2
	2p	3p → 4p	25.3	27.0	20.9
			24.9		20.9
3p	3p → 4p	21.6	24.8		
Kr	3d	4p → 5p	20.4	22.7	18.8
			20.5		18.8
	3p	4p → 5p	20.5	22.7	
			20.2		
4p	4p → 5p	18.4	21.9		
Xe	3d	5p → 6p	16.9	19.0	15.9
			16.9		15.9
	4d	5p → 6p	17.0	18.9	
			16.9		
		16.8			

^aFrom Spears *et al* (1974).

comparison of these eigenvalues with the measured ionisation potentials is not possible.

Shake-up transition energies calculated by the present scheme are compared in table 2 with available experimental and the theoretical Hartree-Fock values of Spears *et al* (1974). The present theoretical results are on the whole close to the experimental values. It is interesting to note that the predicted values are consistently a few eV higher than the experimental results. This is again probably due to the omission of relativistic effects which are typically of the order of 4 eV (Watson and Perlman 1975). This expectation is well borne out by our preliminary results obtained by the solu-

tion of the relativistic HFG equations (Selvaraj and Gopinathan 1982). It may also be pointed out here that the various satellite peaks arising from the multiplet splitting cannot be predicted by the HFG or other X_a type schemes as in these methods the various multiplet states are replaced by a single average state.

Calculated shake-up transition probabilities are given in table 3. They compare well with the experimental as well as theoretical HF values. The only exception is the K_{γ} 4p-5p transition for which the intensity is underestimated. We do not have an explanation for this discrepancy.

Theoretical shake-off transition energies are presented in table 4. Experimental

Table 3. Shake-up intensities in rare gas atoms.

Atom	Ionising level	Transition	Intensity in percentage		
			Exptl. ^a	HFG-STSB	HF ^a
Ne	1s	2p → 3p	8.7	20.8	19.6
			9.6		19.6
Ar	2s	3p → 4p	8±1	12.8	14.6
			8±2		14.6
	2p	3p → 4p	7±1	13.1	15.4
Kr	3p	4p → 5p	7±1	12.1	15.4
			5±1		11.6
	3d	4p → 5p	8±1	2.4	11.5
			8±1		11.5
Xe	3d	5p → 6p	11±1	12.1	12.4
			8±1		12.4
	4d	5p → 6p	6.3	10.2	9.6
			5.1		9.6

^aFrom Spears *et al* (1974); ^bPresent work.

Table 4. Shake-off energies in the rare gas atoms.

Atom	Ionising level	Shake-off level	Shake-off energy in eV	
			HFG-STSA	HFS ^b
Ne	1s	2p	53.7	45.8
	2s	2p	50.8	40.3
	2p	2p	51.0	40.4
Ar	1s	3p	34.0	30.4
	2s	3p	33.6	29.8
	3s	3p	31.5	27.5
	2p	3p	33.7	29.9
	3p	3p	32.4	27.0
Kr	1s	4p	29.1	26.1
	2s	4p	29.0	25.9
	2p	4p	29.0	25.9
	4s	4p	27.4	24.2
	4p	4p	28.1	23.7
Xe	1s	5p	24.8	22.1
	2s	5p	24.8	22.0
	2p	5p	24.9	22.0
	3s	5p	24.7	21.9
	3p	5p	24.7	21.9
	4s	5p	24.7	21.8

^aPresent work; ^bFrom Carlson and Nestor (1973)

values for these transitions have not yet been reported, probably due to difficulties associated with the positive identification of shake-off peaks in ESCA spectra. However results of theoretical calculations using relativistic HFS wavefunctions by Carlson and Nestor (1973) are available and these are also given in table 4. It is seen that the HFG transition state method predicts these transition energies fairly well.

From the foregoing it is clear that the use of the Slater transition state method with HFG wavefunctions is capable of reproducing all the main features of the experimental ESCA spectrum such as the ionisation, shake-up and shake-off energies and shake-up intensities. The attractiveness of the method lies in its computational simplicity. However relativistic corrections appear to be necessary for further improvement of the calculated results.

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