

Determination of parameters of valence states by using XANES

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A new approach for the parametrization of valence states of atoms in molecules and solids, facilitating the deciphering of experimental XANES spectra, is proposed. It is shown that energies and half-widths of XANES maxima of the one-electron origin depend mainly on the arrangement of atoms and energies and mean radii of atomic valence states. Just these quantities having distinct physical meaning must be determined above all from experiment. A procedure for such a determination is developed. Values of energies and mean radii of the nitrogen and oxygen atoms in some molecules are obtained.

Keywords: XANES, valence states

1. Problem

Our aim is to investigate valence states of separate atoms in many-atom systems. Such systems can be molecules, free or adsorbed, solid clusters and so on. This problem is a part of the more general question which we try to examine (Migal, 1994): what information about objects under consideration is contained in XANES and how to extract this information.

Analysing XANES we choose peaks of the one-electron origin. As usual such peaks are the most distinctive details of spectra. They correspond to the transition of the photoelectron to both unoccupied collective states of the discrete spectrum and so called shape resonances. The latter are one-electron quasi-stationary states with small positive energies. We consider only such peaks which correspond to states localized or quasi-localized within many-atom systems (i.e., the Rydberg series is excepted). Position and form of these peaks essentially depend on arrangements and types of atoms, magnetic microstructure, the presence and nature of defects, the distribution of electric charge, etc. This fact allows us, in principle, to obtain structure information by analysing characteristics of the peaks. However, unfortunately, general methods for extracting this information are still not developed.

Before considering concrete questions about atomic valence states we would like to make three general remarks. *Firstly*, an amount of information coded in XANES is essentially greater than in EXAFS. It is caused by the fact that in the case of XANES the photoelectron, moving through a many-atom system with a comparatively small speed, interacts with the system for much longer time than in the case of EXAFS. Due to that, by using XANES it is possible to obtain, along with geometric parameters of the system, also parameters of the potential $V(\mathbf{r})$ describing the interaction between the photoelectron and the system.

Secondly, since position and form of peaks in XANES depend on a lot of factors, in order to extract information from XANES one must solve a many-parameter inverse problem. In a number of works, where for deciphering structure information from XANES

one uses methods of the direct problem solution and restricts oneself to the determination of one or two parameters chosen, this circumstance is not taken into account. For this reason, results obtained in these works are either inaccurate or depend on the subjective interests of the authors.

Thirdly, so long as an amount of experimental data relating to maxima of the one-electron origin in XANES is limited, there is a problem what physical characteristics are determinable by them and what ones are not determinable. Obviously, by using such data it is impossible to construct completely the potential $V(\mathbf{r})$, because for solving such a problem it is necessary to have the infinite set of data. However, one can expect to get via XANES a restricted set of parameters relating to the potential. Our task is to reveal these parameters. From our previous studies (Migal, 1999) it follows that just characteristics of atomic valence states can be such parameters.

In our investigations we use, as experimental data, positions and widths of the peaks. The point is that these quantities are the most reliable from ones measured experimentally. In comparison with them, heights of the peaks are measured to a low precision. Including such inexact quantities in the analysis can lead to essential errors in values of structure parameters examined.

Under such conditions, as we restrict the amount of data only by energies and widths of peaks, it is convenient to use a formalism based on analysis of poles of the S matrix for many-centre systems (Migal, 1993). Within this formalism it is not assumed to employ other quantities besides energies and widths of maxima, and it is balanced in amounts of input and output information. It is known that if in a system there is an one-electron state with a negative energy, there exists a pole of the S matrix in the negative axis of the complex energy plane. If there is a resonant state, it is associated with a pole in the fourth quadrant of this plane (see, e.g., Taylor, 1972). The real coordinate of this pole is equal to the energy E of the resonance, and the imaginary coordinate is equal to the half-width Γ of the corresponding spectral maximum.

If we have values S_{exp} of poles obtained from experiment and possess a model of the many-atom system, then by fitting parameters of the model we can attain the coincidence of values S_{exp} and poles calculated for the model. If such a problem is solved uniquely, one can expect that parameters of the model after fitting approximately correspond to parameters of a real object.

In what follows we describe briefly the method allowing the maximal amount of structure information to be extracted from data of energies and widths of peaks of the one-electron origin in XANES. Data of valence states of separate atoms from many-atom systems are a part of this information. Then we adduce characteristics of these states calculated by the proposed method for the nitrogen and oxygen atoms.

2. Method

We choose the well-known muffin-tin (MT) model as a model which enables us to reproduce basic properties of a real many-atom system in an approximation which is sufficient for us. Within this model the whole aggregate of factors, influencing position and form of the maxima of the one-electron origin, amounts to parameters describing the arrangement of atoms and characteristics of the intratomic potentials. For calculating S -matrix poles we use an

equation in these poles obtained in Migal (1993) within the MT approach

$$\det \left\| \left[1 + i c t g \delta_i^{(j)} \right] \delta_{j' l'} \delta_{L L'} + \sum_{L'} H_{L L' L''}^{j'} h_{l'}^+(k | \vec{r}_j - \vec{r}_{j'} |) \right\| = 0 \quad (1)$$

Here r_j are coordinates of nuclei of the system, δ_i are phaseshifts for separate atoms, $h_l^+(x)$ are spherical Hankel functions,

$$H_{L L' L''}^{j'} = 4 \pi i^{l-l''} Y_{L'}(\vec{r}_j - \vec{r}_{j'}) \int Y_L Y_{L'} Y_{L''} d\Omega$$

are so called structure constants.

It is important that in (1) only the phaseshifts δ_i depend on the potential $V(\mathbf{r})$. This fact will be used below.

The potential within atomic spheres in general case can be written in the form (Migal *et al*, 1997)

$$V_{MT}(r) = V_0(r) + \sum_n b_n r^n (n = 0, 1, \dots) \quad (2)$$

where V_0 is a starting potential which can be chosen in different ways. It may be a square well (the simplest variant), an analytical potential or the standard MT potential obtained *ab initio* by any modern code. Coefficients b_n are parameters varied together with atomic coordinates r_j . Both the coefficients b_n and atomic coordinates are subject to the determination by an iterative procedure.

We begin our calculations by computing a set of poles for a model system with some starting values of varied parameters. Then our task is to decrease the discrepancy between calculated and 'experimental' poles of the S matrix by changing parameters of the model. To this end we minimize the functional

$$\Phi = \sum_i \{ S_{cal}^{(j)} - (E_i - i\Gamma_i/2) \}^2 + \alpha \sum_j (x_j - X_j)^2 \quad (3)$$

where x_j are varied parameters, X_j are their reference values, α is a regularization parameter, $S_{cal}^{(j)}$ are calculated poles, E_j are energies and Γ_j are half-widths of experimental peaks. (The parameter α should be equal to zero if the number of varied parameters does not exceed the number of experimental data.)

Here it is necessary to explain how the spectrum should be treated to get E_j and Γ_j values required for the analysis. Above it was mentioned that we select only peaks of the one-electron origin. In general case the selection of such peaks from all peaks in XANES can be a difficult problem. Methods of the selection of the peaks are described in Migal (1994). The situation is simple if previously a direct problem calculation within the MT approach for a given object was performed (it can be done by means of available codes), and an accordance between experimental and calculated peaks was settled. A divergence remaining between the calculation and experiment can be eliminated or essentially diminished by solving the inverse problem and refining values of structure parameters used in the preliminary calculation.

Determining values of Γ_j it should be taken into account that within the standard MT model the decay of resonant states is caused only by going out of the photoelectron to infinity. Therefore, while processing the spectrum, we must eliminate contributions of all

other mechanisms of the decay. Such mechanisms are: the return of the photoelectron to a core state, the excitation of atomic vibrations, apparatus distortions, etc. To eliminate these effects we act as follows. If in the spectrum there is at least one peak corresponding to the transition of the photoelectron to a state of the discrete spectrum, whose width within the MT approach must be equal to zero, we subtract its width from widths of the rest of peaks. We suppose in this way that all effects, not taken into account within the MT approach, lead, in total, to a widening of peaks which is approximately equal for all peaks under consideration. This assumption is justified because, if in the spectrum there are some peaks corresponding to the transitions to discrete levels, their widths are, as a rule, approximately equal.

It should be emphasized that the set $\{x_j\}$ of variable parameters of a model must be adequate to the problem posed, i.e., all independent parameters influencing spectral characteristics must be included into account. For stabilizing the solution in the case when the number of variable parameters exceeds the number of experimental data, it is necessary to use in (3) reference values X_j taken from calculations of objects which are similar to one being studied. By minimizing functional (3) we obtain a solution of the many-parameter inverse problem of the XANES theory.

We have tested the developed method by considering some simple objects. Results of the test are adduced in Migal (1998). Here, for instance, we represent data of the NO_2 molecule. The internuclear distance $R_{\text{N-O}}$ in this molecule is equal to 1.193 Å, and the valence angle φ_{ONO} is equal to 132°. Analysing the NK spectrum by the proposed method we have determined the next values: $R_{\text{N-O}} = 1.185 \text{ Å}$, $\varphi_{\text{ONO}} = 132.4^\circ$. From results of the test it follows that we really can determine internuclear distances up to 1% and valence angles up to 3%.

In those calculations, together with geometric parameters we also varied parameters of potential. (It was necessary to do because varying only geometric parameters could lead to inexact results.) It was found (and this fact will be important in what follows) that in sums (2) for the potential one can retain only two coefficients b_n per atom, and it is sufficient for reproducing energies and widths of peaks in XANES to a high degree of precision. Moreover, it is possible to retain in (2) any pair of coefficients (for example, b_0 and b_1 , b_0 and b_2 , etc), and results keep the same. This fact is valid for any starting potential V_0 . It is caused by properties of atomic phaseshifts through which characteristics of peaks depend on the potential. The point is that in a narrow energy interval, where peaks of the one-electron origin are situated, the phaseshifts are simple functions of the energy. Namely, the function $\delta_i(E)$ at $E < 2$ Ryd is completely described by two parameters discussed in the next section. (Here we can see the manifestation of the fact that it is impossible to construct uniquely the potential $V(\mathbf{r})$ by using only experimental data of energies and widths of the peaks.)

3. Parameters of potential determined by XANES

In search of parameters characterizing completely the behaviour $\delta_i(E)$ at $E < 2$ Ryd we have obtained as follows. As such parameters for each separate atom of a many-atom system we can choose characteristics of one-electron states with the highest energy: namely, the energy ε_b and the mean radius $\langle r \rangle_b$ of a valence state

(if in an atom there is such a state) or the energy ε_{res} and the half-width γ of a resonant state (if in an atom there is a shape resonance). The behaviour of the phaseshifts in interval from 0 to 2 Ryd for two atoms with identical values of the pairs $(\varepsilon_b, \langle r \rangle_b)$ or $(\varepsilon_{res}, \gamma)$ is practically non-distinct although the form of the potential within the both atoms can be quite different.

From this fact it inevitably follows that the amount of information, relating to the potential and extracted from data of energies and widths of peaks in XANES, is limited by one of pairs of the quantities above mentioned (or any other pair of their functions). It should be emphasized that these pairs of parameters are not observables measured experimentally. They are quantities defined within the MT approach. The main sense of them lies in the fact that they characterize the potential within separate atoms of a many-atom system.

Then we can pose the next problem: how to decipher values of ε_b and $\langle r \rangle_b$ from XANES. To this end we should have some mathematical relation between δ_l and the pair $(\varepsilon_b, \langle r \rangle_b)$. We have found such a relation in an implicit form by using an auxiliary function $F_l = E^{l+1/2}(1 + ic \tan \delta_l^{(l)})$. This function is smooth, and its zeros coincide with ε_b values. Besides, the inclination of the function F_l at the point ε_b is uniquely determined by the value of $\langle r \rangle_b$. The main equation allowing values of ε_b and $\langle r \rangle_b$ to be determined can be written in the form

$$F_l(E, \langle r \rangle + \Delta \langle r \rangle, \varepsilon_b + \Delta \varepsilon_b) = f_l(E, \langle r \rangle, \varepsilon_b) + c_l(\Delta \langle r \rangle) \varphi_l(E) + d_l(\Delta \varepsilon_b) \chi_l(E) \quad (4)$$

where f_l is a notation for F_l with starting values of the parameters ε_b and $\langle r \rangle_b$, φ_l and χ_l are some auxiliary functions independent of these parameters (see Migal, 1999). Coefficients c_l and d_l are new variables determined through minimizing functional (3). Equation (4) is employed within an algorithm worked out for determining parameters ε_b and $\langle r \rangle_b$. Details of this algorithm are described in (Migal, 1999)

4. Results and discussion

By using the method developed we have obtained values of energies and mean radii of 2p states in the MT potential of the nitrogen and oxygen atoms in various molecules (see Table 1). We hope that these results give us some useful information which can be revealed by a subsequent analysis.

Obviously, the quantities ε_b and $\langle r \rangle_b$ corresponding to a chosen atom changes noticeably when we go over from one molecule to others. (This fact is natural even in that case as the environment of the atom changes insignificantly.) The analysis of changes of ε_b and $\langle r \rangle_b$ can be productive if some relations between these quantities and other characteristics of atoms or parameters describing the arrangement of atoms in a system will be found.

Table 1

Energies and mean radii of 2p states of the N and O atoms obtained by XANES (upper index '+' corresponds to positive ions).

Atom	Molecule	ε_b , Ry	$\langle r \rangle_b$, a.u.
N	N ₂	-0.172	1.320
N	NN ⁺	-0.760	1.070
N ⁺		-1.323	0.991
N ⁺	N ⁺ O ₂	-1.086	1.015
O		-0.903	1.085
O	S ⁺ O ₂	-0.942	1.079
O	OO ⁺	-0.651	1.168
O ⁺		-1.342	1.061
O	OO ⁺ adsorbed on Cu(100)	-0.379	1.260
O ⁺		-1.027	1.098

We suppose that the discovered dependence of δ_l on ε_b and $\langle r \rangle_b$ and also some consequences of this dependence are, maybe, somewhat unexpected. One of the consequences lies in the fact that within the MT approach energies of collective valence states in a many-atom system are completely determined by the atomic arrangement and values of energies and mean radii of valence states of separate atoms of the system. The same set of the quantities determines energies and widths of spectral maxima corresponding to transitions of the photoelectron to collective resonant states of the system.

Of course, the dependence of energies of collective valence states on energies of states of separate atoms is not a surprise. But the fact that energies of collective states are determined completely only by the atomic arrangement and pairs of the quantities ε_b and $\langle r \rangle_b$, we think, is unexpected. In this connection, one can assume that the quantities ε_b and $\langle r \rangle_b$ might be used for describing chemical bonds in various compounds. These quantities have a distinct physical meaning and can be determined more distinctly than some notions used traditionally in quantum chemistry, for example, effective atomic charges and overlapping integrals.

In conclusion, it is worth to note that the idea about the role of the pair $(\varepsilon_b, \langle r \rangle_b)$ has appeared as a consequence of the general approach to the solution of the inverse problem in XANES theory.

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