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Theory of x-ray absorption spectra of central atoms in high-symmetry molecules and complexes

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On the basis of the reflection-matrix concept introduced by the authors earlier, the formation of near-threshold singularities in x-ray absorption spectra are investigated. The conditions for the onset of resonances in a many-center potential are determined. Formulas are derived for the energies and intensities of the lines of the Rydberg-series when a molecular state is superimposed on the latter. A criterion for the separation of molecular and Rydberg levels is proposed. For the SF_6 molecule, the matrix of reflection from the fluorine octahedron and the x-ray absorption spectra of sulfur are calculated. The results are compared with experiment.

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INTRODUCTION

X-ray absorption spectra (XAS), as is well known, make it possible to obtain important information on the structure of matter. The far fine structure of the spectra makes it possible to determine the coordination number, the distances to the nearest atoms, and the amplitudes of the thermal vibrations.[1,2] From the characteristics of the Rydberg series observed before the threshold of the continuous absorption it is possible to establish the charges of the ions and the symmetry of the nearest surrounding.[3] These effects in the XAS are caused mainly by the scattering of the photoelectron in the final state by potentials localized in the region of space adjacent to the absorbing atom. The scattering of an electron wave by surrounding atoms, which is sometimes described by specifying modified boundary conditions for the wave function on the surface of the investigated atom or group of atoms,[4] plays at any rate a very important role in the formation of the local electron density (LED) in matter. Without a detailed investigation of the singularities of this scattering and without revealing the role of the bearest and remote surroundings it is impossible to make serious progress in the understanding of the electron structure of defects in crystals, amorphous bodies, or liquids.

A number of authors have shown[5-8] that calculations of the XAS intensities by the method of multiple scattering in the $\chi-\alpha$ approximation[9] gives results that are in satisfactory agreement with experiment. There is no doubt now that this method makes it possible to describe quantitatively both the far and the near fine structure of the XAS. The calculations, however, do not explain qualitatively the causes of the singularities in the spectra and cannot separate the role of the potentials of the nearest surroundings and of the atom to which the x-ray transition takes place.

In this paper, using a new procedure recently proposed by us[10,11] to describe the influence of the surrounding potentials on the LED and on the XAS intensity, we carry out a systematic analysis of the role of the nearest surrounding in the formation of the local electron structure. We investigate the XAS and LED of central atoms of high-symmetry close-packed molecules, complexes, and clusters, and pay principal attention to the formation of the fine structure at the absorption edge. We consider the laws governing the onset of resonances in a many-center potential and of the theory of the Rydberg series in the presence of molecular states near this series.

It is known that to solve our problem we can use the muffin-tin (MT) potential approximation.[9] In this approximation the potentials inside the intersecting atomic spheres are assumed to be spherically symmetrical. (In the multiple-scattering method it suffices to specify in lieu of these potentials only the phase shifts δ_l of the scattering by them.) The potential between the atomic spheres is assumed to be constant and is taken in this paper to be the zero point. In the case of a fine system of atoms, such as a molecule, a complex, or a cluster, the potential outside the large-radius sphere that includes the entire system (the Watson sphere) is also assumed to be spherically symmetrical. At infinity, this potential tends to a constant value designated V_{vac} ($V_{\text{vac}} \geq 0$).

1. MATRIX OF REFLECTION OF AN ELECTRON WAVE BY SURROUNDING ATOMS

The intensity of the x-ray spectrum of the absorption of unpolarized radiation by an electron situated on a deep level with binding energy E_0 and wave function $g_l(\mathbf{r})$ can be written in the form[10]

$$I(E) \approx -\int \operatorname{Im} G(\mathbf{r}, \mathbf{r}', k)\, \mathbf{r}\mathbf{r}' g_l(\mathbf{r}) g_l(\mathbf{r}')\, d^3r\, d^3r', \tag{1}$$

where[1)] $k = (E - E_0)^{1/2}$ is the wave number, and $G(\mathbf{r}, \mathbf{r}', k)$ is the Green's function of the electron in the final state. (The functions $g_l(\mathbf{r})$ are chosen real.)

The presence of the rapidly decreasing function $g_l(\mathbf{r})$ under the integral sign limits the volume of integration to the internal region of the atomic sphere, in which the *MT* potential is spherically symmetrical. Inside this sphere, the dependence of $\operatorname{Im} G(\mathbf{r}, \mathbf{r}', k)$ on the coordinates can be easily separated in explicit form:

$$\operatorname{Im} G(\mathbf{r}, \mathbf{r}', k) = \sum_{l,m,l',m'} \operatorname{Im} G_{lm,l'm'}(k) \chi_{lm}(k, \mathbf{r}) \chi_{l'm'}(k, r'), \tag{2}$$

where $\chi_{lm}(k, \mathbf{r})$ is the regular solution of the Schrödinger equation in the potential of only one atomic sphere, and is normalized to $\delta(E - E')$.[2)]

It is clear that the coefficient $G_{LL'}(k)$ depends both on the potential of the central atom and on the potential outside the atom. To ascertain the role of the potentials of the surroundings, we introduce an auxiliary irregular solution of the Schrödinger equation $f_{(L)}(k, \mathbf{r})$ with a potential equal to zero in the intra-atomic region of the center in question, and left unchanged outside the region. We specify for this solution the boundary conditions in the form

$$f_{(L)}(k, \mathbf{r}) = \begin{cases} h_l^{(1)}(kr) Y_L(\mathbf{r}) + \sum_{L'} R_{LL'}(k) h_{l'}^{(2)}(kr) Y_{L'}(\mathbf{r}) & \text{at} \quad r < r_0, \\ \sum_{L'} D_{LL'}(k) h_{l'}^{(1)}(kr) Y_{L'}(\mathbf{r}) & \text{at} \quad r \to \infty, \end{cases} \tag{3}$$

where $h_l^{(i)}(x)$ are Hankel functions of the first and second kind and r_0 is the radius of the central atomic sphere.

The quantity $R_{LL'}$, henceforth called the matrix element of the reflection matrix **R**, depends only on the potential situated outside the atomic sphere of the absorbing center, and has a rather clear physical meaning. This is the amplitude of a converging wave $h_{l'}^{(2)}(kr)$ with an angular dependence $Y_{L'}(\mathbf{r})$, reflected from the ligands, in the presence of a wave $h_l^{(1)}(kr)$ emerging from the center and having an angular dependence $Y_L(\mathbf{r})$. Similarly, the quantities $D_{LL'}$ have the meaning of transmission amplitudes.[12,13] As shown in[12], the matrix **R** is symmetrical and if only elastic processes are taken into account it satisfies a condition analogous to the unitarity condition

$$\mathbf{R}\mathbf{R}^{+} + \mathbf{D}\mathbf{D}^{+} = 1. \tag{4}$$

Equation (4), which is a consequence of the flux conservation, imposes on the matrix element $R_{LL'}$ and $D_{LL'}$ important *a priori* limitations that do not depend on the concrete form of the potentials of the ligands. Satisfaction of this equality is a test of the correctness of the approximate calculations of the matrix **R** and restricts the range of variation $|R_{LL'}| \leq 1$.

The connection between the coefficients $G_{LL'}$ and $R_{LL'}$ can be established by comparing in the region of the central atomic sphere the expansions, in cubic harmonics, of the solution $f_{(L)}(k, \mathbf{r})$ [formula (3)] and of the Green's function calculated in the same potential as $f_{(L)}(k, \mathbf{r})$, and by taking subsequently the central potential into account with the aid of the Dyson equation[12]:

$$\mathbf{G} = i(1 + \mathbf{S}\mathbf{R})(1 - \mathbf{S}\mathbf{R})^{-1}, \tag{5}$$

where $S_l = \exp(2i\delta_l)$ is the S matrix of scattering by the central atomic sphere.

Using the selection rules for the dipole transition, we write down with the aid of (1)–(5) an expression for the absorption K-spectrum (the formula for the L-spectrum can be written analogously[13]):

$$I(E) = \left[\int g_0(\mathbf{r})\, \mathbf{r} \chi_1(k, \mathbf{r})\, d^3r\right]^2 \operatorname{Re} \sum_{m=1}^{3} [(1 + \mathbf{S}\mathbf{R})(1 - \mathbf{S}\mathbf{R})^{-1}]_{1m,1m}. \tag{6}$$

Formula (6) is exact, but its analysis in the general case is difficult, and we therefore consider in the present paper only the case of a diagonal **R** matrix. It takes place for a cubic symmetry in the basis of cubic harmonic we confine ourselves to inclusion of $l \leq 2$ on the central atoms. We shall henceforth use the notation

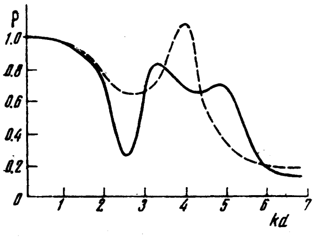

FIG. 1. Modulus of the reflection amplitude from an octahedral surrounding $\rho(f_{1u})$, calculated exactly (solid line) and in first-order pertrubation theory in the scattering multiplicity (dashed). The phase shifts of the scattering by the ligands do not depend on the energy, $\delta_0 = 0$, 1π, $\delta_1 = 0$, 5π.

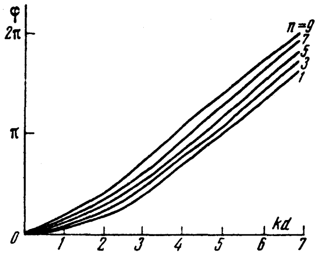

FIG. 2. Phase shift of the amplitude of reflection from a cubic surrounding $\varphi(a_{1g})$. The phase shifts of the scattering by the ligands do not depend on the energy, $\delta_0 = 0$, $\delta_1 = n\,0,1\pi$ (the number n is marked on the curve).

$$\left[\int g_l(\mathbf{r})\mathbf{r}\chi_{l'}(k,\mathbf{r})d^3r\right]^2 = M^2_{ll'}$$

$$\operatorname{Re}\left[(1+\mathbf{SR})(1-\mathbf{SR})^{-1}\right]_{LL} = P_L(E),$$

$$R_{LL}(E) = \rho_L(E)\exp(2i\varphi_L(E)),$$

where ρ_L and φ_L are real.

If there are no ligands, then $\mathbf{R} = 0$ and formula (6) takes on the usual form of the XAS intensity of an isolated center. Thus, the quantity $P_L(E)$ describes the change of the XAS under the influence of the potential of the ligands and coincides by definition with the local partial density of states.

Even in the diagonal case, the dependence $\mathbf{R}(E)$ can be investigated analytically only in the asymptotic regions $kd \ll 1$ and $kd \gg 1$ (d is the radius of the system). To investigate the most interesting intermediate region kd we calculated the reflection matrices of octahedral and cubic surroundings for the irreducible representations a_{1g} ($l = 0$ on the central atomic sphere), f_{1u} ($l = 1$), and also e_g and f_{2g} ($l = 2$) at $kd < 7$ and all possible phase shifts δ_0 and δ_1 for scattering by the potentials of the surrounding atomic spheres, assuming that $\delta_l = 0$ at $l \geq 2$. The calculations have shown the following:

a) At $kd > 6$ first-order perturbation theory in the scattering multiplicity is quantitatively in good agreement with the exact results, thus confirming the correctness of the use of this perturbation theory in the calculation of the far fine structure of the XAS.

b) At $2 < kd < 6$ first-order perturbation theory does not agree quantitatively with the results of the exact calculations, and even yields unphysical values $\rho > 1$, but accounts qualitatively correctly for their variation (Fig. 1).

c) In the region $kd < 2$ the value of ρ is close to unity for almost all values of δ_0 and δ_1. This is due to the large values of the spherical Neumann functions of small arguments.

d) In the region $kd > 2$ the value of ρ usually begins to decrease, but at $3 < kd < 5$ one frequently observes a maximum or a step on the $\rho(E)$ plot (Fig. 1) at fixed δ_0 or δ_1. This phenomenon, as can be seen, appears already in first-order perturbation theory. Analysis shows that it is due to the suppression of the wave that emerges from the internal region of the atomic system on account of interference between the primary wave and the wave resulting from its scattering by the surrounding. This effect is very important, since it leads to $\rho > 0.5$ in the essential region of the variation of δ_0 and δ_1 up to $kd \approx 5$.[12] The appreciable value of ρ contributes in turn to the onset of sharp maxima in the XAS and LED at these values of kd.

e) The dependence of φ on kd at fixed phase shifts δ_0 and δ_1 is almost linear at $kd > 2$ (Fig. 2), with $\partial\varphi/\partial kd \approx 1$. At $kd < 1$ the value of φ is small at all values of δ_0 and δ_1.

f) The rate at which ρ_L and φ_L tend to their limiting values as $kd \to 0$ increases with increasing l. It can be shown that in this region the following asymptotic formulas are valid:

$$\rho_L = 1 + a_1 k^{4l+2} + a_2 k^{4l+4} + \ldots, \quad a_1 < 0,$$
$$\varphi_L = b_1 k^{2l+1} + b_2 k^{2l+3} + \ldots. \tag{7}$$

Thus, the phase of the reflection matrix has at low energy the same order in k as the ordinary scattering phase.

2. RESONANT STATES IN A MANY-CENTER POTENTIAL

In the continuous-absorption region, the most characteristic details of the spectrum are the resonant maxima, and the attention paid to their study is therefore natural. The first attempt to explain the cause of the maxima in the XAS of the SF_6 molecule was based on the molecular-orbital method.[14] Nefedov[14] introduced the concept of a pseudopotential barrier surrounding the central atom. This concept was further developed in a two-well model[15,16] which made it possible to explain qualitatively some characteristic details of the absorption spectra of molecules of the type SF_6, BF_3, and others. Of late, the study of resonant states in molecules is based on the method of multiple scattering.[5-8] Calculations of the generalized phase of scattering by a molecule show that the phase increases rapidly in the regions of the resonances. However, even in the case of pronounced maxima in the XAS, the discontinuity of the generalized phase in the resonance region can be noticeably smaller than π, the partial scattering cross section need not necessarily reach its unitary limit, and the maximum of the XAS is not always connected with the maxima in the cross section for the scattering of an electron by a molecule.

The concept of reflection matrix makes it possible to explain quite simply and illustratively the nature of the resonances in a many-center potential. The calculations performed show that the most widespread cause of such resonances is the abrupt growth of $P_L(E)$ in the vicinity of the point E_0 at which the following condition is satisfied[13]:

$$\delta_l(E_0) + \varphi_L(E_0) = s\pi, \quad s = 0, 1, 2, \ldots. \tag{8}$$

For a sharp resonance to appear at this point it is necessary merely that the reflection amplitude ρ_L be not less than 0.3–0.4. Physically, the condition (8) means that in the internal region of the atomic group there is formed a standing wave whose intensity is higher the larger the amplitude of the reflection of the wave from the surrounding. It is important to note that in the considered case the resonant behavior of the quantity $P_L(E)$ takes place at smooth energy dependences of all the parameters ρ, φ, and δ which enter in formula (6) for this quantity.

If we neglect the energy dependence of ρ_L on the section $|E-E_0|<\Gamma$, and approximate $\varphi_L(E)+\delta_l(E)$ by a linear function, then $P_L(E)$ takes in the vicinity of E_0 the form of a Lorentz curve:

$$P_L(E)=\frac{A}{\pi}\frac{\Gamma}{(E-E_0)^2+\Gamma^2} \tag{9}$$

with a half-width

$$\Gamma=\frac{1-\rho}{2\rho^{1/2}}\left[\frac{\partial}{\partial E_0}(\varphi(E_0)+\delta(E_0))\right]^{-1} \tag{10}$$

and integral intensity

$$A=\frac{1+\rho}{2\rho^{1/2}}\left[\frac{\partial}{\partial E_0}(\varphi(E_0)+\delta(E_0))\right]^{-1}. \tag{11}$$

By continuing analytically the quantity $(1+SR)(1-SR)^{-1}$ to the complex E plane, we can verify that in the case of resonance it has a pole on the unphysical sheet near the real axis:

$$\frac{1+SR}{1-SR}=\frac{i}{\pi}\frac{A}{E-E_0+i\Gamma}. \tag{12}$$

Formulas (8)–(12) remain valid also for $\rho=1$. In this case the pole turns out to lie on the real axis, $P(E)=A\delta(E-E_0)$, and the resonance is transformed into a bound state.

If we take into account the variation of ρ with energy, then the obtained curve is contracted on the side of lower ρ with an asymmetry index[17]

$$a=1+\frac{3}{(1+\rho)\rho^{1/2}}\frac{\partial\rho}{\partial E}\left[\frac{\partial(\varphi+\delta)}{\partial E}\right]^{-1}. \tag{13}$$

The maximum of the curve is then located at the point E_0':

$$E_0'=E_0+\frac{1-\rho}{8\rho}\frac{\partial\rho}{\partial E}\left[\frac{\partial(\varphi+\delta)}{\partial E}\right]^{-2}. \tag{14}$$

A possible, but according to calculations rare, cause of the onset of maxima in the XAS is the sharp decrease and subsequent rapid growth of ρ. This situation can occur in a solid in the vicinity of narrow forbidden bands.

If it is assumed that $\delta(0)+\varphi(0)=0$, then the condition (8) can be at first satisfied in the region $E>0$ either at $s=0$ or at $s=1$. (The case $s=-1$ is not realized, inasmuch as at the resonance point we have $\partial(\varphi+\delta)/\partial E>0$.[13]) The first situation can occur if one of two conditions is satisfied:

a) C is a large positive quantity in the low-energy expansion of the phase[18]

$$k^{2l+1}\operatorname{ctg}\delta_l=-1/C+rk^2/2. \tag{15}$$

This behavior of the phase corresponds to the presence of a shallow bound state in the central potential.

b) C is small, and the coefficient b_1 in the expansion (7) is negative and is large in absolute value.

The case $\delta(E_1)+\varphi(E_1)=\pi(s=1)$ can be realized also under two typical conditions:

c) the phase shift δ increases sharply in the considered energy interval. This behavior of the phase occurs when a low-energy resonance exists on the central potential.

d) The phase φ increases rapidly at low energies and a rather sharp maximum of the quantity $P(E)$ is observed even at $\delta=0$.

In cases a) and c) one can assume that the resonance is produced in the system because of the existence of either a coupling or a resonance on an isolated potential of the central atomic sphere, and it changes energy and width under the influence of the ligand potential. In cases b) and d) the resonance is formed by the potential of the ligands, and the potential of the central atom only changes its characteristics. It is clear that the considered cases are extreme and in fact it is not always possible to indicate unambiguously the "initiator" of the resonance.

Calculations show that if the phase shifts of the scattering by the ligands have smooth energy dependences, the situation d) is realized quite rarely. For all the phases δ_0 and δ_1 considered above, the quantity φ turned out to be negative at low energies in the irreducible representations e_g and f_{2g} of the octahedron and cube, respectively. (Those are the irreducible representations in which the maxima of the electron density are directed to the largest degree to the atoms of the surrounding.) In the representation f_{1u} of the octahedron, φ is negative only in a certain region of variation of the variables δ_0 and δ_1. Thus, in the absence of a central atom the presence of a low-energy resonance in the system when δ_0 and δ_1 have smooth dependences on the coordinates seems to reflect more readily the geometry of the arrangement of the surrounding atom, rather than the properties of their potentials.

As already noted, in cases a) and c) the maximum in the XAS of the entire system is the result of the existence of a line in the XAS of a single central potential. Let us see to what degree such line characteristics as the width, position, and integral intensity are preserved. Consider the case c). The resonant variation of the phase shift δ corresponds to expansion of the matrix element S near the point E_0 in the form[18]

$$S(E)=\tilde{S}(E)\frac{E-E_0-i\Gamma}{E-E_0+i\Gamma}, \tag{16}$$

where $\tilde{S}$ is the potential part of the S matrix, and is a smooth function of the energy in the vicinity of the point E_0. The square of the matrix element of the transition on the central atom has here a Lorentz form

$$M^2(E)=A\frac{\Gamma}{(E-E_0)^2+\Gamma^2}. \tag{17}$$

If the center in question is placed inside an atomic system with a reflection matrix R, then the XAS intensity can be obtained from formula (6). Putting

$$SR=R', \quad \frac{1+R'}{1-R'}=\Delta$$

and approximately assuming R' to be a quantity independent of energy, we get, substituting (16) in (6),

$$P(E)=\operatorname{Re}\Delta\frac{(E-E_0)^2+\Gamma^2}{(E-E_0-\Gamma\operatorname{Im}\Delta)^2+(\Gamma\operatorname{Re}\Delta)^2}. \tag{18}$$

From this we get

$$I(E)=A\frac{\Gamma\operatorname{Re}\Delta}{(E-E_0-\Gamma\operatorname{Im}\Delta)^2+(\Gamma\operatorname{Re}\Delta)^2}. \tag{19}$$

It is seen from formula (19) that the energy of the resonance is shifted by an amount $\Gamma\mathrm{Im}\Delta$, the half-width takes on the value $\Gamma\mathrm{Re}\Delta$, and the integral intensity remains the same as before. At $\rho=1$ the quantity Δ becomes imaginary and

$$I(E)=A\delta(E-E_0-\Gamma\operatorname{Im}\Delta), \tag{20}$$

i.e., the resonance is transformed into a bound state.

Obviously, the foregoing analysis remains in force also for a clearly pronounced resonance in a molecule or a complex when the latter are placed inside a large atomic system.

It should be noted that there are quite frequent cases in which R' cannot be regarded as constant over an energy interval of the order of Γ. The presence of a resonance of this sort on the central potential can induce a resonance in the entire system, realizing the condition (8), but the result that its integral intensity remains unchanged turns out to be incorrect. As will be shown in Sec. 4, this situation takes place in the SF_6 molecule, in which a weakly pronounced resonance at $l=2$ on the potential in the atomic sphere of sulfur induces two sharp intense maxima in the irreducible representations e_g and f_{2g}.

In case a), which is realized in the region of low levels, it can also be shown that the integral intensity of the resonance is equal to the integral intensity of the bound state that has generated it, if this state is sufficiently well localized in the central atomic sphere.

3. RYDBERG SERIES IN HIGH-SYMMETRY MOLECULES

If the system remains positively charged after the emission of a photoelectron, then the potential outside the Watson square (WS) contains a Coulomb part and a characteristic Rydberg series appears in the absorption spectrum.[3] Experiment shows that the intensity of this series is strongly suppressed in molecules with large coordination numbers.[19] In the potential-barrier model, this suppression is attributed to the small penetrability of the barrier that separates the center of the molecule from the region of localization of the Rydberg states.[16] For a correct reduction of the experimental data it is necessary to know the form that the spectrum possesses if, as is frequently the case, a molecular state is superimposed on the Rydberg series (RS), and how to classify correctly the spectral lines in this case.

To solve this problem we find first the amplitude of the reflection of an electron wave from a potential behind the WS. In the region of interest to us, near the vacuum zero, we can use a quasiclassical approximation that yields good results in a Coulomb potential at low energies. In this approximation, the radial Schrödinger equation takes the form

$$\psi_l''+(k^2-V(r)-\lambda^2/r^2)\psi_l=0, \tag{21}$$

where $\lambda=l+1/2$.

We reckon the potential $V(r)$ from the potential in the interatomic region (the MT zero). Then at $r<r_w$

$$V(r)=0, \tag{22a}$$

and as $r\to\infty$

$$V(r)\to V_{\mathrm{vac}}-2Z/r, \tag{22b}$$

where r_w is the radius of the WS and $V_{\mathrm{vac}}>0$.

It is clear that at $k^2<V_{\mathrm{vac}}$ we have $\rho=1$. To find the phase of the reflection amplitude we need the value, at $r=r_w$, of the quasiclassical wave function ψ_l that tends to zero at infinity[21]:

$$\psi_l(k,r_w)=(p_l(r_w))^{-1/2}\sin\left\{\int\limits_{r_w}^{r_R}p_l(x)\,dx+\frac{\pi}{4}\right\}, \tag{23}$$

where $p_l(x)=[k^2-V(x)-\lambda^2/x^2]^{1/2}$, and r_R is a turning point that is far from the origin.

We integrate the argument of the sine function by parts, recognizing that $p_l(r_R)=0$:

$$\int\limits_{r_w}^{r_R}p_l(x)\,dx=-p_l(r_w)r_w-\int\limits_{r_w}^{r_R}x\frac{dp_l}{dx}dx. \tag{24}$$

We put $\varkappa^2=V_{\mathrm{vac}}-k^2$. As $\varkappa\to0$, the first two terms of the asymptotic expansion of the integral in the right-hand side of (23) in powers of $\varkappa$ takes the form

$$\int\limits_{r_w}^{r_R}x\frac{dp_l}{dx}dx=-\frac{Z\pi}{\varkappa}+\nu_l\pi. \tag{25}$$

The quantity ν_l in this expansion depends on the concrete form of the potential $V(r)$ and on the WS radius.

To find the reflection amplitude it is necessary to represent the wave function (23) on the WS in the form

$$\psi_l(k,r_w)=Ckr_w[h_l^{(1)}(kr_w)+R_{LL}(k)h_l^{(2)}(kr_w)]. \tag{26}$$

It follows therefore that

$$\varphi_l=\frac{Z\pi}{\varkappa}-\nu_l\pi+\frac{\pi}{4}-\frac{\pi l}{2}=\frac{Z\pi}{\varkappa}+\eta_l\pi. \tag{27}$$

If an atomic potential with a scattering phase shift δ_l that can be regarded as constant in the considered energy is situated inside the WS, then from the condition for the existence of bound states (8) it is easy to derive the usual formula for the energy levels in the RS:

$$E_n = V_{\text{vac}} - \frac{Z^2}{(n-\eta_l-\delta_l/\pi)^2}. \tag{28}$$

Assuming approximately that the transition matrix element is independent of the energy, we obtain from (27) and (11) an expression for the integral intensity of the investigated lines:

$$A_n \approx \frac{Z^2}{(n-\eta_l-\delta_l/\pi)^3}. \tag{29}$$

We consider first the question of the formation of the Rydberg series on the central atom of the molecule. We use the formula for the XAS intensity of an atom surrounded by two concentric potentials[12]—the potential of the atoms of the nearest surrounding and the potential outside the WS:

$$I(E) = M^2 \operatorname{Re}\frac{1+SR_1}{1-SR_1} \operatorname{Re}\frac{1+S'R_2}{1-S'R_2}, \tag{30}$$

where

$$S' = e^{2i\delta_l'} = \exp\left\{2i\left[\delta_l + 2\theta_L + \operatorname{arctg}\frac{\rho_L \sin 2(\varphi_L+\delta_l)}{1-\rho_L\cos 2(\varphi_L+\delta_l)}\right]\right\}, \tag{31}$$

R_1 and $D_1 = de^{2i\theta}$ are the reflection and transmission matrices for the nearest atomic surrounding, and $R_2 = \exp(2i\varphi_2)$ is the matrix of the reflection from the potentials past the WS.

The condition for the existence of a bound state (8) can be rewritten in our case in the form

$$-\operatorname{tg}\psi = \frac{\rho\sin 2(\varphi+\delta)}{1-\rho\cos 2(\varphi+\delta)} \tag{32}$$

where

$$\psi = \delta + \varphi_2 + 2\theta.$$

The character of the obtained spectrum depends qualitatively on whether or not there exists, in the group of atomic potentials situated inside the WS, a resonant state in the considered energy region. If not, the phase δ' can be regarded as constant as $E \to V_{\text{vac}}$, and formula (28) for the energy levels remains in force. On the other hand in the expression for the absolute line intensities there appears a factor

$$\operatorname{Re}\frac{1+SR_1}{1-SR_1},$$

which is small in the entire considered region and depends little on the energy by virtue of our assumption that there are no resonances. This factor suppresses the RS in the considered class of molecules.

If a resonance exists near V_{vac} in the internal group of atoms, then the phase δ' in its vicinity can no longer be regarded as constant, and to calculate the level energies it is necessary to use Eq. (32). Let the resonance be characterized by an energy E_0, a half-width Γ, and an integral intensity A. We expand the right-hand side of (32) in powers of $E - E_0$ and retain the linear term:

$$\frac{\rho\sin 2(\varphi+\delta)}{1-\rho\cos 2(\varphi+\delta)} \approx \frac{2\rho}{1-\rho}\frac{\partial(\varphi+\delta)}{\partial E}(E-E_0) = \frac{\rho^{1/2}}{\Gamma}(E-E_0). \tag{33}$$

If E_0 lies close enough to V_{vac}, then in an energy interval of the order of the width of the resonance the phase φ_2 can change very little. The character of the solution of the equation is clear in this case from Fig. 3. In each interval (x_i, x_{i+1}) there exists only one solution. Since the entire region of variation of the energy is of the order of the width of the resonance, it follows that $|E - E_0|/\Gamma \lesssim 1$ and we can approximately replace $-\tan\psi$ inside each integral by a linear function of the energy:

$$-\operatorname{tg}\psi \approx -\beta_i(E-y_i), \quad \beta_i > 0. \tag{34}$$

The energy E_i of a level situated in the i-th interval is then determined from the equation

$$\rho^{1/2}(E-E_0)/\Gamma = -\beta_i(E-y_i). \tag{35}$$

Its solution is of the form

$$E_i = y_i + \frac{E_0 - y_i}{1+\beta_i\Gamma/\rho^{1/2}}. \tag{36}$$

We see therefore that the solutions condense, so to speak, near the point E_0 and do not fit the usual Rydberg series.

To find the integral intensity of the line A it is necessary to divide the function

$$M^2 \operatorname{Re}\frac{1+SR_1}{1-SR_1},$$

which has by assumption the form (9), by the derivative

$$\frac{\partial(\varphi+\delta)}{\partial E} \approx \frac{\partial\psi}{\partial E} + \frac{\partial}{\partial E}\operatorname{arctg}\frac{E-E_0}{\Gamma}\rho^{1/2}. \tag{37}$$

The resultant quotient is

$$\frac{A_i}{\pi} = A\Gamma/\pi[(E_i-E_0)^2+\Gamma^2]\left[\beta_i + \frac{\Gamma\rho^{1/2}}{\rho(E_i-E_0)^2+\Gamma^2}\right]. \tag{38}$$

It is obvious that if

$$\beta_i \ll \frac{\Gamma\rho^{1/2}}{\rho(E_i-E_0)^2+\Gamma^2}$$

then $A_i \to A$. On the other hand if E_i is far from E_0, then

$$\beta_i \gg \frac{\Gamma\rho^{1/2}}{\rho(E_i-E_0)^2+\Gamma^2}$$

and

$$A_i \to \frac{A}{\pi}\frac{\Gamma}{(E_i-E_0)^2+\Gamma^2}A_i', \tag{39}$$

where $A_i' = 1/\beta_i$ is the integral intensity of the RS line (27).

It is seen from (38) that if the point E_0 lies near Y_i, then one of the spectral lines will be much more intense than the others, and if on the other hand the point E_0 is close to x_i, then the spectrum will contain two intense neighboring lines. The physical nature of the singularities in both cases is the same—the presence of a resonant state in a system without a potential outside the WS. It is possible in this connection, with physical justification, to subdivide the states lying above the MT zero into molecular and Rydberg states. Molecular states can be defined as levels that go over into sta-

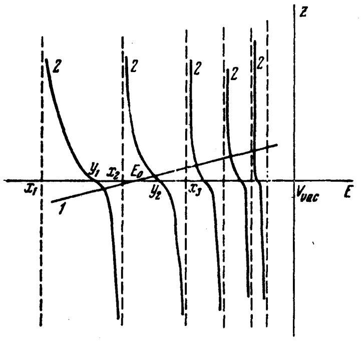

FIG. 3. Graphical solution of Eq. (31); curve $1-z = (E-E_0)\rho^{1/2}/\Gamma$, $2-z = -\tan\psi$.

tionary states of the potential past the WS is made to tend to zero. The remaining lines in the spectrum can be called Rydberg lines, since their existence is due only to the potential past the WS. It must be remembered however, that for a correct reduction of these states it is necessary to use not formula (28) but formulas (36) and (38).

4. CALCULATION OF REFLECTION MATRIX FROM FLUORINE OCTAHEDRON IN THE K and $L_{2,3}$ ABSORPTION SPECTRA OF SULFUR IN THE SF_6 MOLECULE

A good illustration of the developed methods is provided by calculations of the R matrix and the XAS in the SF_6 molecule. This molecule is a well investigated object, to which a large number of studies, both experimental and theoretical, have been devoted.[5,6,14,16,22] Its XAS is characterized by the presence of narrow intense maxima above the continuous absorption, by a strongly suppressed RS, and by the absence of a jump on the absorption threshold.

We used in our calculation the phase shifts for scattering by the potentials in the atomic spheres of sulfur and fluorine, obtained as a result of a self-consistent calculation of the ground state of the molecule by the multiple-scattering method in the X-α approximation. The radius of the atomic sphere of the sulfur was assumed in this calculation to be 1.762 a.u., and the

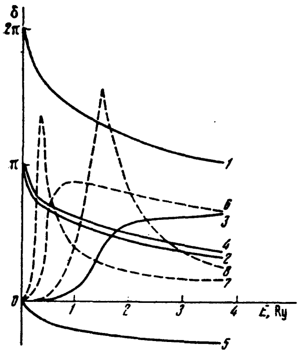

FIG. 4. Phase shifts of scattering by atomic spheres of sulfur and fluorine in the SF_6 molecule (solid lines), probabilities of transitions on an isolated atomic sphere of sulfur in the same molecule (dashed). The probabilities of the transitions are given in different relatige units. The energy is reckoned from the MT zero. $1-\delta_0^S$, $2-\delta_1^S$, $3-\delta_2^S$, $4-\delta_0^F$, $5-\delta_1^F$, $6-M_{10}^2$, $7-M_{01}^2$, $8-M_{12}^2$.

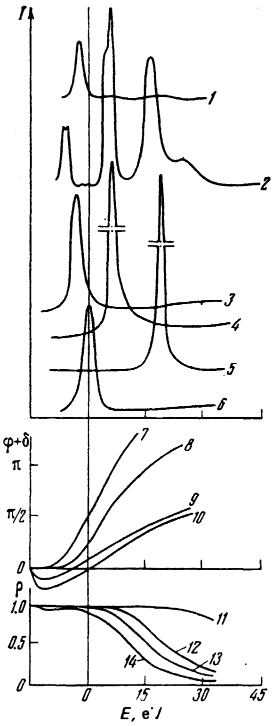

FIG. 5. Calculations of intensities of the transitions and of the reflection matrix in the SF_6 molecule: 1, 2—K and $L_{2,3}$ absorption spectra of sulfur,[20] 3 $3-I(a_{1g})$, $4-I(f_{2g})$, $5-I(e_g)$, $6-I(f_{1u})$, 7 · $7-\varphi(f_{2g})+\delta_2^S$, $8-\varphi(e_g)+\delta_2^S$, $9-\varphi(a_{1g})+\delta_0^S$, $10-\varphi(f_{1u})+\delta_1^S$, $11-\rho(e_g)$, $12-\rho(a_{1g})$, $13-\rho(f_{1u})$, $14-\rho(f_{2g})$. All diagrams are drawn to the same energy scale. The vertical bar denotes the ionization threshold.

fluorine sphere radius 1.244 a.u. The ionization threshold turned out to be 1.1 Ry higher than the average interatomic potential chosen to be the origin. The energy dependences of the scattering phase shifts and of the matrix elements of the transition are shown in Fig. 4. The plots of the quantities $\rho_L, \varphi_L+\delta_l$, and I_L calculated by us are shown in Fig. 5 together with the experimental spectrum. The calculations were made for the irreducible representations $a_{1g}(l=0), f_{1u}(l=1), e_g$, and $f_{2g}(l=2)$. It is seen from Fig. 5 that φ_L and ρ_L are smooth functions of the energy. In all four irreducible representations the condition (4) turned out to be satisfied in the region of large ρ. In the representations a_{1g} and f_{1u} this was due to the large s and p scattering lengths of the sulfur (case a) of Sec. 2). In the representations e_g and f_{2g} the resonant behavior of the phase δ_2 of the sulfur came into play at $E=1.5$ Ry (case c) of Sec. 2). This resonance turned out to be quite weak, so that the maximum in the matrix element of the transition is quite broad, and the jump in the phase amounted to only 1.7. None the less, it was precisely this jump which induced the very sharp intense maximum in $P(e_g)$ and $P(f_{2g})$, which lie above the threshold of the continuous absorption. The calculated ratio of the integral intensities of the maxima in $P(e_g)$ and $P(f_{2g})$ is 1.5, which agrees well with the experimental value 1.3.

The potential situated beyond the WS, which was not taken into account in our calculation, had little effect on the behavior of the spectra above the threshold of the continuous absorption because of the smallness of the coefficient of reflection from it. On the other hand, the resonances in the representations a_{1g} and f_{1u}, which are located below the threshold, were transformed under the influence of this potential into bound states with the same integral intensity (see Sec. 2), observable in the K and $L_{2,3}$ spectra. The RS and the jump on the absorption threshold turned out to be suppressed because of the low penetrability of the fluorine octahedron for the electron wave in this energy region.

In conclusion, a few remarks concerning the line width. The experimentally observed widths of the maxima corresponding to bound states in the representations a_{1g} and f_{1u}, turn out to be respectively of the order of 1 and 3 eV. These widths are due to multielectron effects and to apparatus distortions, which were not taken into account in our analysis. The very same effects contribute also to the experimentally observed resonance widths. It follows from our calculations that the widths corresponding to the departure of the electron to infinity are of the order of 0.2 and 0.1 respectively for the representations f_{2g} and e_g, i.e., they are appreciably less than the observed widths of the bound states. This explains the similarity of the line widths in the discrete and in the continuous parts of the spectrum in molecules of this class.

The experimental value of the width of a resonance with high energy (representation e_g) is of the order of 3 eV, whereas the width of the low-energy resonance is 1 eV. This increase of the resonance width at a relatively small increase of its energy can be attributed to two causes. First, the maxima of the electron density in the e_g representations are directed towards the fluorine atoms, and not towards the intervals between them as in the f_{2g} representation, and consequently the amplitudes of the Auger processes on the fluorine atoms in the e_g representation should be substantially larger. Second, the width corresponding to the departure of the electron to infinity turned out to be very small because of the anomalously large reflection amplitude in the e_g representation, this being due to the fact that the maxima of the electron wave are directed exactly towards the atoms of the surroundings. The reflection amplitude in this representation should be very sensitive to small displacements of the atoms from the equilibrium position. Therefore the thermal vibrations of the molecules can decrease the reflection amplitude in this channel and consequently increase the width of the resonant state.

The RS levels having a low integral intensity are in a special situation. The electrons on these levels are localized behind the nearestatomic surrounding, where the electron density is small. This leads to a sharp decrease of the probability of the Auger processes. Therefore the indicated lines are much narrower than the states localized in the internal region of the molecule.

CONCLUSION

In our preceding papers,[12,13] with an aim at investigating the role of the ligands in the formation of the near-threshold singularities of the XAS, we proposed to introduce a matrix $R_{LL'}$ whose elements are the reflection amplitudes of the electron waves having different orbital angular momenta and radiated out of the investigated center. In the present article, on the basis of a calculation of the matrix of the reflection from the octahedral and cubic surroundings at $l \leq 2$ (the matrix $R_{LL'}$ for the central atom is diagonal in this case), we carried out a systematic analysis of the physical nature and the conditions for the onset of the principal near-threshold singularities of the XAS—of the resonances and of the Rydberg series—for central atoms in the investigated high-symmetry systems. We have shown the following: The reflection amplitude R_{LL} varies as a rule slowly with changing energy in the case when the phases shifts of the scattering by the ligand potentials are smooth functions of the energy.

The main cause for the appearance of sharp maxima in the XAS is the satisfaction of the phase condition (8) in the case when the amplitude of the reflection from the surrounding is large enough ($\rho_L = |R_{LL}| > 0.3$). Such resonances arise even in the case of smooth energy dependences of R_{LL} and δ_l, and are due to the formation of a standing wave in the internal region of the atomic system. The amplitude of this wave with increasing ρ. In the case when $\rho = 1$, the resonance is transformed into a bound state. The large value of ρ in the considered cases is typical of a large class of ligand potentials in the region $kd < 6$.

Resonance on the central potential, as a rule, induces resonance in the entire system. At values of ρ close to unity this resonance is more strongly pronounced than the bare one. If the resonance on the center is well formed (the phase discontinuity is close to π), then its integral intensity is not changed when the center is placed in the atomic system. An analogous situation obtains when a shallow bound state is present on the central potential.

The calculation carried out for the SF_6 molecule shows that the onset of all the maxima in the XAS of sulfur is due to the causes listed above. The calculation results agree well with experiment.

The reflection-matrix method applied to the theory of the Rydberg series makes it possible to explain simply and illustratively the decrease of its intensity on account of the potentials of the nearest surroundings, and also obtain formulas that give the positions and intensities of the RS lines, if a molecular state is superimposed on this series. The presented analysis allows us to define the molecular state as a state that goes over into a resonant state when a potential past the Watson sphere is turned on.

The existence of such states, which are formed mainly because of the strong reflection of the electron wave from the nearest environment, is an important fact that must be taken into account in the analysis of the long-range order and of the formation of LED in a solid. One can expect that the cluster approach, which has been extensively used of late to calculate the electron structure of defects in crystals,[23] will give good results for that part of the LED which is due to the indicated states.

An approach based on introduction of a reflection matrix can be used to study the LED and XAS of atoms in infinite systems. Although there is as yet no effective method of calculating the reflection matrix, one can hope that it will remain a smooth function of the energy and can be specified with the aid of a small number of parameters.

In conclusion, the authors are grateful to A. P. Kovtun for providing the results of the calculations of the electron structure of the SF$_6$ molecule. The authors thank V. P. Sachenko and A. P. Kovtun for a discussion of the manuscript.

1) The energy is measured in this paper in Rydbergs, and the remaining quantities are given in the atomic system of units.

2) We use here real spherical functions, the so-called cubic harmonics.[11] Therefore m does not have the meaning of the magnetic quantum number, and merely numbers harmonics with a definite value of orbital angular momentum $(m=1, 2, \ldots, 2l+1)$. The symbol L denotes the pair of numbers (l, m). Bearing in mind that all the calculations are carried out in this paper in a definite irreducible representation of the point group of the system, corresponding to the chosen L on the central atom, we shall hereafter frequently omit the index L, or replace it by the symbol of the irreducible representation.

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Effects of the Landau-Zener type in the optical spectra of molecules

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We investigate the influence of nonadiabatic coupling of electron-vibrational terms of molecular systems on their optical properties. It is shown that Landau-Zener effects in the vicinity of the quasicrossing of the terms lead to a substantial restructuring of the energy spectrum, to beats in the absorption line intensities, and to asymmetry in the absorption and emission spectra. Typical objects in which the predicted singularities can be observed are indicated. The case of laser-induced quasicrossing of terms is considered separately.

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When a theory is developed for the theory of electron-vibrational optical spectra of molecular systems it is important to take into account the fact that the excited term to which the transition is realized is as a rule not isolated and has regions of approach (quasicrossing) with the ground-state or some other excited terms in configuration space of the molecule. A special role can be played here by quantum states that result from the nonadiabatic coupling of the terms in the quasicrossing region. The coupling of the term can be due to electron-vibrational interaction, to spin-orbit coupling, or to mixing of these states by external laser radiation (induced quasicrossing).

If the matrix element of the coupling of the terms is comparable in magnitude with the characteristic distance between the vibrational conditions, then a sub-

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