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Collective response and molecular effects in cluster photoionization: A one-center time-dependent calculation for BaO_2

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We calculate the photoionization cross section of a BaO_2 molecule in the region of the Ba $4d$-f giant dipole resonance, i.e., 90–150 eV, taking into account both many-electron screening and molecular, multiple scattering effects. The potential of the oxygen ligand atoms is expanded in spherical harmonics around the central Ba atom and screening is treated within the time-dependent local-density approximation. The cross section shows prominent modulations and structure due to final-state molecular resonance effects, in good qualitative agreement with experimental results on solids.

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The collective and single-electron response of clusters has become an intensely studied subject in recent years, both experimentally and theoretically, with applications to metallic clusters [1], C_{60} [2], and high-T_c superconductors [3]. Moreover, with the development of materials physics and surface physics there is a strong general interest in the electronic structure and dynamics of embedded atoms and molecules [4].

The field is, however, of longstanding interest: synchrotron radiation soft-x-ray absorption spectra of solid xenon [5] and Ba halogenides [6] show prominent oscillations of the $4d$-εf giant dipole continuum resonance [7] in the 100-eV region. The dynamics of this resonance involves the entire atomic $4d$ shell, i.e., the resonance is collective and essentially atomic [8], but the final continuum states involve molecular resonances due to multiple scattering and interference effects. During the recent studies of the electronic structure of high-T_c superconductors using synchrotron radiation, a number of spectra of the Ba $4d$-f giant resonance in YBaCuO have been measured using photoemission techniques [9]. These results [6,9] very clearly demonstrate a prominent broad collective resonance with prominent oscillations of the cross section. In this paper, we shall demonstrate that a similar effect is evident in calculations on a simple model system, linear BaO_2 with bond lengths taken from $YBa_2Cu_3O_7$.

The oscillatory structure in photoionization cross sections gives information about the local environment around the photoemitting atom, such as distances to ligands, coordination, etc. This is well known and exploited in photoabsorption and photoemission from deep core levels [extended x-ray-absorption fine structure (EXAFS), near-edge x-ray-absorption fine structure (NEXAFS), surface extended x-ray-absorption fine structure (SEXAFS), x-ray appearance near-edge structure (XANES) [10]], where the photoionization process may be reasonably well described within a one-electron picture and where the atomic background level can easily be determined by inspection. However, in the valence and inner-valence low-energy region, say 0–200 eV, the structural information is much more difficult to extract due to nontrivial variation of the "background" due to screening and other many-electron effects.

In this paper we present a model calculation which takes into account both many-electron screening and molecular effects for a heavy atom, Ba, "embedded" inside a one-dimensional oxygen "cage," BaO_2 (i.e., a linear O—Ba—O molecule). Here we give results for the photoionization cross section in the region of the Ba $4d$-f giant dipole resonance, centered around 110 eV. Many-electron screening is taken into account via the time-dependent local-density approximation (TDLDA) [11,12] and the oxygen ligands are described through one-center expansion [12] around the central Ba atom.

In one-center expansions the molecular problem reduces to an atomic problem, but with coupled angular-momentum channels [12–15]. The TDLDA therefore becomes a matrix equation in the angular variables and a differential equation in the radial variable. The problem with the method is that very high angular momenta are needed to describe the ligand atoms with reasonable accuracy: the l expansion is rather slowly convergent and unable to describe the nuclear singularities of the ligands. The advantage is that the Coulomb interaction can be calculated in a straightforward way. Hence electron-electron correlation and many-particle dynamics in the cluster can be studied using well established many-body techniques for atomic systems. In this way, Levine and Soven [12,13] were able to achieve quite good agreement with experiment for the $3\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\pi_u \rightarrow 1\pi_g$ channels in N_2 and C_2H_2, which demonstrated the importance of induced screening fields in the $3\sigma_g$ and $1\pi_u$ bonds.

In this paper we demonstrate that the method can also

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be applied with good results to molecules or clusters with a heavy central atom and a shell of fairly light ligands, e.g., transition and rare-earth metal oxides. We present the first results for the soft-x-ray absorption spectrum of the linear O-Ba-O molecule (Ba-O distance 5.064 a.u.; from YBaCuO) in the frequency range 90–150 eV, i.e. in the region of the Ba $4d$-εf giant dipole resonance. In these first calculations we model the O-Ba-O molecule using superposition of atomic potentials (Fig. 1) and use this non-self-consistent molecular potential to calculate bound and continuum states and Green functions. This will describe basic effects of molecular bond formation, covalency, and charge transfer. It will also describe basic effects of multiple scattering and shape resonances. However, due to the lack of self-consistency of the electronic structure, we are only dealing with a model system and a model calculation.

To calculate the electronic structure of the BaO_2 cluster we expand the initial bound-state wave functions and the final continuum state Green functions in spherical harmonics [13],

$$\psi(\mathbf{r})=\frac{1}{r}\sum_L u_L(r)Y_L(\Omega) , \tag{1}$$

$$G(\mathbf{r},\mathbf{r}';E)=\sum_{L,L'} Y_L(\Omega)G_{LL'}(r,r';E)Y^*_{L'}(\Omega') , \tag{2}$$

and obtain a set of coupled Schrödinger equations involving angular-momentum expansion $V_{LL'}(r)$ of the nonspherical potential $V(\mathbf{r})$. [$L=(l,m)$ is a compact notation for the two spherical harmonic indices.] These equations are solved by procedures described in Refs. [13,14].

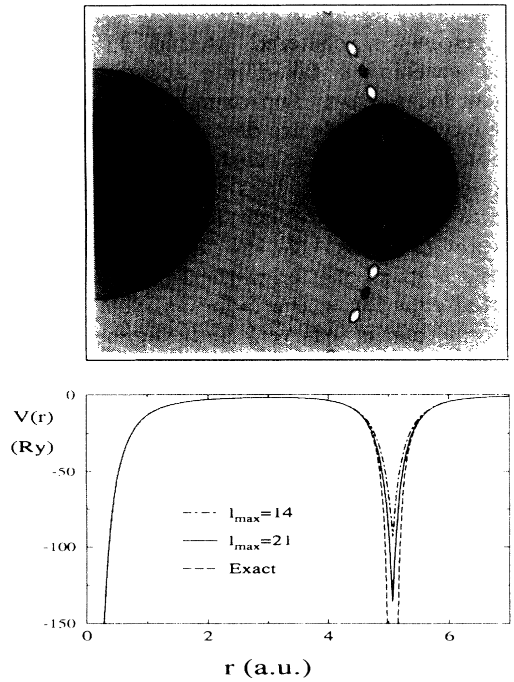

FIG. 1. Pictures of the O-Ba-O potential (superposed atoms): (a) contour plot; (b) along the Ba-O axis, $l_{max}=14$, 21, and exact.

In the present calculation we have to truncate the l expansion of the wave function in Eq. (1) at $l_{max}=21$ [which implies including potential l components $V_{LL'}(r)$ up to $l=42$], dictated by the limited accuracy and range of the Cray computer (maximum 128-bit words in double precision).

From the initial-state wave functions and the final-state Green functions we then construct the dielectric susceptibility, calculate the induced charge $\delta n(\mathbf{r};\omega)$ in a self-consistent manner within the TDLDA and finally obtain the photoabsorption cross section

$$\sigma(\omega)=-4\pi\alpha a_0\omega \mathrm{Im}\int z\delta n(\mathbf{r};\omega)d\mathbf{r} , \tag{3}$$

where $z=r\cos\theta$ is the component of the electric dipole operator along the O-Ba-O axis, α is the fine-structure constant (1/137), and a_0 is the Bohr radius.

Figure 2 shows the result for the total photoionization cross section of our O-Ba-O cluster ($l_{max}=21$) together with the result for the cross section of the *superposed* atoms, Ba+2O. The electric-field vector is parallel to the O-Ba-O axis. We note that the oxygen ligands do not modify the overall strength and shape of the Ba $4d$-f giant dipole resonance: the effect is to induce a structure which oscillates around the atomic "background." These oscillations of the cross section must be associated with molecular, multiple scattering effects (shape resonances) and cannot be described in terms of EXAFS and single scattering.

Figure 3 shows the variation of the cross section when l_{max} is increased from $l_{max}=14$ to $l_{max}=21$. In a very important sense our results are well converged: the variations with l are much more severe for $l_{max}<14$ and extend over a wider range. For $l_{max}\geq 14$ the variations are confined to a fairly narrow range of energies and the basic two-peak structure does not change much: the amplitude of the oscillations increases and there is a slight shift towards threshold with increasing l_{max}. This may be understood in the following way: with increasing l_{max}, the central part of the oxygen potential gets deeper, as indicated in Fig. 1. This will pull down and sharpen the oxy-

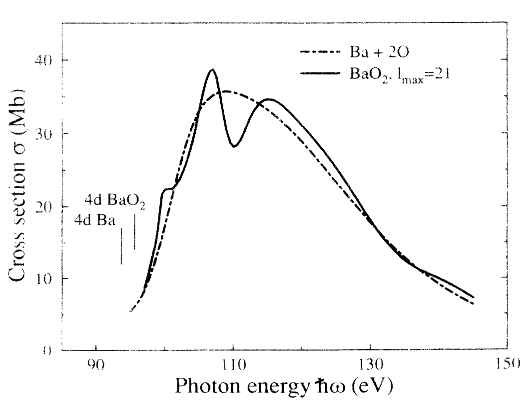

FIG. 2. Photoabsorption cross section of the O-Ba-O (BaO_2) cluster. Solid line: present results for $l_{max}=21$. Dashed-dotted line: superposition of atomic Ba+2O to represent the average cross section without multiple scattering (O atoms also calculated using one-center expansion with $l_{max}=21$).

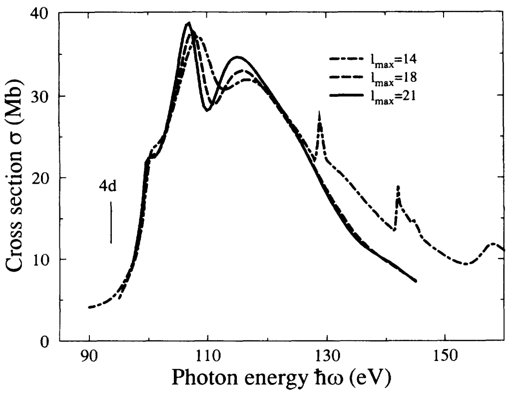

FIG. 3. Photoabsorption cross section of the O-Ba-O (BaO_2) cluster for $l_{\max}=14$ (dashed-dotted line), $l_{\max}=18$ (dashed line), and $l_{\max}=21$ (solid line). The structures above 125 eV are due to O1*s* absorption, appearing at much too low energies for $l_{\max}=14$ because of lack of depth of the O potential (see Fig. 1).

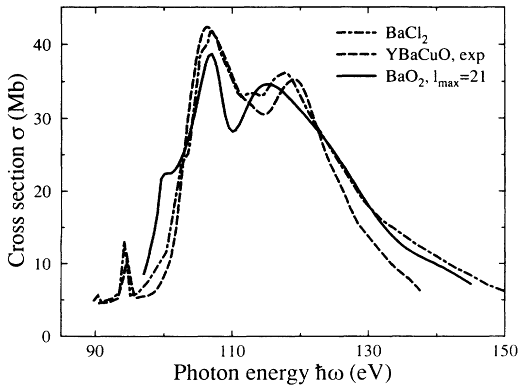

FIG. 4. Photoabsorption cross section of the O-Ba-O (BaO_2) cluster for $l_{\max}=21$ (solid line), together with experimental results for $YBa_2Cu_3O_7$ [9(d)] (dashed line) and $BaCl_2$ [6] (dashed-dotted line). The cross section scale for the experimental curves is arbitrary and the fitting is qualitative (due to background subtraction).

gen resonances somewhat by making the oxygen continuum wave functions more localized, contracting the central part. Moreover, Fig. 1 shows that the limited *l*-expansion results in a ligand potential which is too wide in the angular direction. This should partly compensate for the lack of depth in the radial direction. Therefore, in spite of the limited convergence of the *l* expansion, we expect the peak structure in the photoabsorption cross section in Fig. 3 to be significant. The use of a non-self-consistent-field (SCF) ground state is a moderate perturbation in this context, and cannot be expected to change the qualitative results. As a consequence, with a limited (but high) *l* expansion, one can hope to describe the low-energy structure quite well (the high-energy oscillations should however damp out because of "lack of singularity" of the outer well).

The result of the calculation makes sense in a very important way. Since the O_2 cross section is small in this frequency range (a few Mb), the essential feature is the modification of photoelectron emission from the atomic Ba 4*d*-*f* giant dipole resonance by scattering from the oxygen ligand potentials. These modifications should not change the integrated oscillator strength of the Ba 4*d*-*f* resonance (which is concentrated to the frequency range shown in Fig. 2). We then note, by inspection, that the BaO_2 and the atomic Ba+2O cross sections in Fig. 2 have the same area, corresponding to the same number of effective Ba 4*d* electrons.

In Fig. 4 we compare with experimental photoyield data for BaO_2 in the form of the high-T_c superconductor $YBa_2Cu_3O_7$ [9(d)] (we do not know of similar data for BaO_2 solid or gas; Y and Cu only provide a smooth, slowly decreasing background [3(c)]). A general kind of agreement is guaranteed because the atomic giant dipole resonance dominates the cross section. Concerning the molecular oscillating structure, there is qualitative agreement in the sense that theory also produces a dominant two-peak structure, although the splitting seems too small.

This splitting, however, can vary considerably between different systems. To indicate the experimental range of qualitative features, we also show photoabsorption data for *solid* $BaCl_2$ [6] in Fig. 4. It is fair to say that the present results agree even better with $BaCl_2$ for which the splitting of the major peaks is smaller and there is a peak on the rising edge around 100 eV. Comparison with other systems, e.g., solid BaF_2 and $BaBr_2$ [6], confirm this view. We therefore arrive at the following general picture: (i) the basic double-peak structure arises from transmission through the ligand potential well, is common to all systems and spectra, and is relatively easy to obtain theoretically; (ii) the size of the splitting and the character of the fine structure depends on the details of the ligand potential and may be relatively difficult to reproduce in the calculation.

One should regard the present calculation as a model calculation demonstrating that very reasonable results can indeed be obtained. For serious comparison with experiment, on the other hand, the system under investigation must be treated in a more realistic manner, irrespective of the issue of convergence of the *l* expansion. For *free molecules* one should start the calculation from a proper (self-consistent) description of the molecular charge density and potential. Moreover, one may have to consider atomic configuration interaction of the type $4d^{-1}4f \leftrightarrow 4d^{-1}5p^{-1}5d^{2}$ [16] (2*h*-2*e* configurations are not included in the TDLDA) in order to properly describe the tendency of the atomic cross section to peak around 120 eV. Also, one should consider coordinations such as BaO_4 and BaO_6 to describe heavy metal ions inside ligand cages, with applications to rare-earth and actinide halide vapors and perhaps also to solid-state environments. Strong coordination can only enhance the oscillatory structure. TDLDA calculations for BaC_{60} [2e] (Ba at the center of C_{60}, representing "maximal coordination") produce results similar to Fig. 2 of the present paper, and even more similar to the experimental YBaCuO result in Fig. 4.

Finally, in order to characterize the oscillatory structure one could try to find an effective one-electron wave function, observing resonance behavior in real space, or studying phase-shift variations with photoelectron energy. The TDLDA many-electron technique does not produce effective wave functions. However, one can approximately express the result for the dominating $4d$-f channel in terms of a one-electron-like problem with an effective, energy-dependent, f-electron potential which radically differs from the one-electron LDA potential [8] and which produces very different phase shifts. The oscillations of the cross section must be associated with additional nodes of this one-electron continuum f function moving into the valence region outside the Ba core, corresponding to resonant localization in the oxygen outer wells, or to resonant scattering against the oxygen ligands. Work along these lines is in progress and will be reported elsewhere.

In conclusion, we have applied a TDLDA one-center expansion to a model of a linear O-Ba-O (BaO_2) molecule in order to study the combined effects of dynamic screening, molecular bond formation, and multiple scattering on the collective Ba $4d$ giant dipole resonance centered around 110-eV photon energy. Our results show that the giant resonance becomes modulated by a spectrum of peaks, in good qualitative agreement with experiment. We interpret the structures in terms of molecular resonances and resonant transmission through the potential of the ligands.

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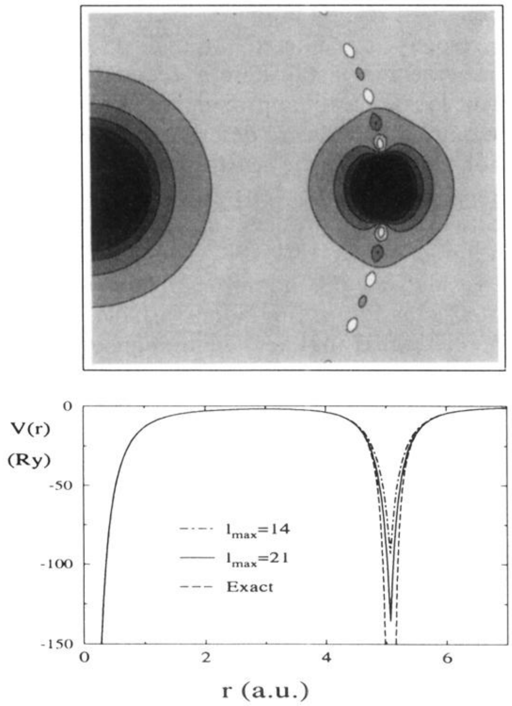

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