MULTIPLE SCATTERING THEORY OF PHOTOELECTRON ANGULAR DISTRIBUTIONS FROM ORIENTED DIATOMIC MOLECULES

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We use multiple scattering photoelectron diffraction (MSPD) theory to calculate the angular patterns of electrons photoemitted from the K-shell of CO and N₂ gas-phase oriented molecules, as recently measured by several groups. For low (E<50 eV) kinetic energies of the photoemitted electron, the electron scattering cannot be adequately represented by spherically symmetric potentials. We thus include nonspherical scattering potentials in our formalism through nondiagonal scattering matrices. We show that intramolecular scattering and interference are responsible for the experimentally measured patterns. This MSPD approach represents a more accurate and versatile method for dealing with such angular distributions as compared to prior calculations of these effects.

1. Introduction

Angular distributions of electrons photoemitted from oriented molecules have become an exciting new tool for studying electronic structure and dynamics.¹-³ Experimental techniques based on coincidence measurements have only recently allowed measuring the orientation in space of the molecule at the very precise instant in which each electron is photoemitted. A reasonable assumption supporting this kind of measurements is that the typical rotation times of the molecule are much larger than the time needed for the molecule to dissociate.

Experimental coincidence techniques have dramatically increased the amount of information that can be extracted from the photoemission spectra, since the angular patterns are not averaged over different orientations of the molecule. Photoemission spectra from fixed-in-space molecules were previously available only for molecules adsorbed on surfaces. However, in the latter case, the measured electronic properties include effects derived from the chemical binding of the molecule to the surface, and the photoemitted electron is affected by the underlying surface. The study of photoemission spectra from gas-phase oriented molecules thus represents a giant step ahead in the field.

The theoretical analysis of the photoemission angular patterns from oriented diatomic molecules has usually been based on works⁴,⁵ that used multiple scattering theory between the two centers of the molecule to calculate the photoemitted electron wave function at the detector position. Only recently have some authors tried to improve this description by using more sophisticated models.⁶,⁷ Multiple scattering theory in spherical potentials provides a correct physical picture of the process under study, but requires rough approximations for the potentials from which the photoelectrons scatter. The standard
muffin tin description does not reproduce some of the details of the potential that are important for low electron energies.\(^8\)

In this work, we keep the advantages of the multiple scattering picture and overcome its limitations by including nonspherical scattering potentials. A similar approach was used by Foulis \textit{et al}. for the calculation of photoionization cross sections of molecules.\(^9\) Multiple scattering in nonspherical cells\(^10\) requires the calculation of the wave function in every single nonspherical cell, in order to obtain the nondiagonal scattering T-matrices.\(^11\) The latter play the role of the diagonal T-matrices based on phase shifts in standard multiple scattering theory.

We apply our model to the calculation of angular distributions of photoelectrons emitted from the K-shell of diatomic molecules, such as CO and N\(_2\). We will show that multiple scattering theory provides an accurate description of the electron photoemission and subsequent diffraction processes.

Atomic units are used in the following, unless otherwise stated.

2. Theory

The theoretical model has been described elsewhere,\(^8\) and it is only summarized here. The OZ axis of our system of coordinates is along the axis of the diatomic molecule. For a given kinetic energy of the electron \((E = k^2/2)\), the photoelectron intensity at the detector position \(I(r_d)\) is proportional to the square of the photoemitted electron wave function \(\Psi(r)\) evaluated at \(r_d\) (for practical purposes, the detector can be considered to be at infinity):

\[
I(r_d) \propto |\Psi(r_d)|^2, \quad \text{as } r_d \to \infty .
\]

From time-dependent first-order perturbation theory, the final state of the photoemitted electron can be obtained from

\[
\Psi = \hat{G} \hat{V}_{\text{rad}} \phi_i ,
\]

where \(\phi_i\) is the initial state of the electron in the molecule (in the present case, a core state), \(\hat{V}_{\text{rad}}\) is the incident light operator and \(\hat{G}\) is the Green operator of the full system:

\[
\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{T}_{\text{mol}} \hat{G}_0 .
\]

\(\hat{T}_{\text{mol}}\) is the scattering operator of the molecule. It can be formally expressed in terms of the total molecular potential \(\hat{V}_{\text{mol}}\) in which the photoemitted electron moves:

\[
\hat{T}_{\text{mol}} = \hat{V}_{\text{mol}} + \hat{V}_{\text{mol}} \hat{G}_0 \hat{T}_{\text{mol}} . \quad (4)
\]

In the latter equations, \(\hat{G}_0\) is the free electron Green operator.

The molecular potential in real space \(V_{\text{mol}}(r)\) is split into two different nonspherical cells. The size of these cells is limited by the internuclear distance. No intracell vector is larger than the distance between the two nuclei of the molecule. This restriction in the size of the cells implies that we are neglecting the effect of the potential Coulomb tail at long distances. However, the local effect of the Coulomb hole is included in the potential. The treatment of the Coulomb tail will be discussed elsewhere.\(^12\) \(V_{\text{mol}}(r)\) is calculated as the sum of an electrostatic term (by using the Hartree–Fock wave functions of the neutral molecule, and without populating the core hole), plus a local exchange term.\(^13\)

The splitting of the molecular potential into two cells allows us to use multiple scattering theory\(^14\) to obtain \(\Psi(r)\). The total scattering operator of the molecule \(\hat{T}_{\text{mol}}\) can be obtained as a function of individual-cell scattering operators \(\hat{T}_i\). For each energy, the wave function outside the cells is expanded in terms of outgoing Hankel functions\(^15\) \(h_l^+(kr)\):

\[
\Psi(r) = \sum_{i=A,B} \sum_L \rho^i_L h_l^+(k|r-r_i|)Y_L(\Omega, r-r_i) ,
\]

where the index \(i\) refers to atoms \(A\) and \(B\) of the molecule, \(Y_L(\Omega)\) are spherical harmonics and the indices \((l, m)\) are grouped in a single index \(L\). The coefficients \(\rho^i_L\) have to be determined. Continuity of the wave function at the boundaries of the cells imposes the following multiple scattering conditions:

\[
\rho^i_L = [\rho^i_L]_0 - ik \sum_{L_1, L_2} \rho^{i}_L T_{L_1 L_2}^{i} G_{L_1, L_2}^{i} \rho^{j}_L . \quad (6)
\]

The index \(i\) is different from \(j\). The sums over \(L_1\) and \(L_2\) are truncated after convergence with the number of \(L\'s\) has been achieved. The matrices \(G_{L_1, L_2}^{ij}\) are coefficients in the expansion of Hankel functions about a different center, and are given by

\[
G_{L_1, L_2}^{ij} = 4\pi i^{l_1-l_2} \sum_{L_3} i^{l_3} h_{l_3}^+(k|r_i-r_j|) Y_{L_3}(\Omega, r-r) \times \int d\Omega Y_{L_1}(\Omega) Y_{L_2}^*(\Omega) Y_{L_3}(\Omega) . \quad (7)
\]
$T^i_{L',L_1}$ are the matrix elements of the scattering $T_i$ operator. They include all necessary information about the electron scattering in the nonspherical potentials $V^i(r)$.

The multiple scattering system of equations Eq. (6) is solved by matrix inversion, so that the coefficients $\rho^i_{L}$ are calculated in a single self-consistent step. The coefficients $[\rho^i_{L}]_0$ in Eq. (6) are the coefficients of the wave function before the intramolecular scattering takes place. In the dipole approximation, these coefficients are calculated from the corresponding matrix elements.\textsuperscript{14} They do depend on the light polarization vector.

The coefficients $\rho^i_{L}$ provide us with all necessary information about the intramolecular scattering. They describe the behavior of the wave function at infinity and are sufficient to calculate the total intensity $I$ for any given position of the detector $r_d$:

$$I(r_d) \propto |\Psi(r_d)|^2_{r_d \to \infty}$$

$$\propto \frac{1}{(kr)^2} \left\{ \sum_i e^{-ikr} \sum_L (-i)^{l+1} \rho^i_L Y_L(\Omega_{r_d}) \right\}^2 . \quad (8)$$

After calculating the coefficients $\rho^i_{L}$, the wave function $\Psi(r)$ of Eq. (5) can be expanded in terms of Hankel functions centered at a single site. The coefficients of this expansion are equivalent to the angular coefficients that are commonly used to fit the experimental angular patterns.\textsuperscript{2,3}

3. Results and Discussion

We previously analyzed the role played by the Coulomb hole in the photoemission angular patterns of oriented CO molecules.\textsuperscript{8} In this article, we focus our attention on the comparison between the theoretical results that can be obtained using our theoretical model and available experimental data on oriented diatomic molecules.

The angular distributions of electrons photoemitted from CO and N\textsubscript{2} molecules have been studied in detail by several experimental groups.\textsuperscript{1\textendash}3,16,17 Particularly important are the energies for which shape resonances appear in the continuum. At these energies, there is a maximum in the total photoemission cross section and the photoelectron angular distributions show radical changes.

A typical example of this is the angular distribution of electrons photoemitted from the K-shell of C in the CO molecule, when the incident light is linearly polarized and the polarization vector is parallel to the molecular axis. For kinetic energies of the electron below and above the shape resonance, the electron intensity along the C direction is higher than the electron intensity along the O direction. However, at the shape resonance energy, this behavior is reversed, and the photoelectron intensity is higher along the direction of the O atom.

The theoretical calculation of the photoelectron angular distribution for this case is shown in Fig. 1, together with the experimental data obtained by Weber et al.\textsuperscript{17} The kinetic energy of the photoelectrons is at the shape resonance. Notice that the preferred angle of photoemission for this case is 0° (the O position). The lobes that appear in the photoemission pattern for several other angles are the consequence of combining different partial wave components. We have checked that a maximum value of partial waves of $l_{\text{max}} = 4\textendash5$ usually suffices to describe the angular patterns in this range of energies. The shape resonance thus implies special conditions of scattering for which the direct and the diffracted waves combine to create constructive interference along the O direction.

When the molecule is homonuclear, the theoretical description of the photoemission process is more
complex, partly because of the small energy difference between different initial states. For example, in the case of the N2 molecule, there are two different energy levels (a symmetrical gerade state and an antisymmetrical ungerade state) for the K-shell electrons. The energy difference between these two levels is roughly $\approx 100 \text{ meV}$. As a consequence, experimental spectra usually measure the incoherent sum of the photoemission patterns from both states.

We show in Fig. 2 the angular distribution of electrons photoemitted from the K-shell of the N2 molecule. As in the CO case, we consider photoelectrons with kinetic energy at the shape resonance. Two different theoretical patterns are plotted in Fig. 2: the photoemission pattern from the K-shell gerade state and the photoemission pattern from the K-shell ungerade state. The incoherent sum of both patterns is shown in the figure as well. The latter sum is in good agreement with the experimental data of Weber et al., indicating that the experimental spectra include contributions from both initial states.

4. Conclusions

We have shown in this work that multiple scattering in nonspherical potentials very accurately describes the photoemission angular patterns of gas-phase oriented diatomic molecules. The inclusion of nonspherical potentials allows us to preserve the attractive physical picture of standard multiple scattering theory while overcoming the limitations introduced by spherical cells. Among the advantages of the theory, we should also mention that a single calculation of the multiple scattering coefficients $\rho_L^s$ [Eq. (6)] suffices to obtain the photoemission intensity at any given direction of space, and for any given polarization of the light. The calculation is thus fast and efficient from the computational point of view, and specially adequate for obtaining photoemission angular patterns at a given energy.

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