Photodetachment of O−
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Introduction

The photodetachment of O− (2p6 3P0) has been investigated with a new R-matrix code [1], where we use a B-spline basis for the continuum function functions of the B-spline basis ensures that no single correction is needed for the R-matrix elements. Another distinguishing feature of the present R-matrix calculation is the use of non-orthogonal orbitals for constructing the target wave functions and generating the scattering function. This allows us to employ highly correlated target wave functions without any inconsistency between the continuum and bound parts of the close-coupling expansion. We conducted a detailed investigation regarding the dependence of the photodetachment cross sections on the scattering model and the accuracy of the target description. Target wavefunctions

The target states of neutral oxygen were generated with the B-spline box-based close-coupling method [2]. The corresponding close-coupling expansion has the structure

\[ \psi_{\text{target}}(r) = \sum_{\ell \neq m} C_{\ell m} \psi_{\ell m}^{\text{core}}(r) + \sum_{\ell = m} C_{\ell \ell} \psi_{\ell \ell}^{\text{core}}(r) + \sum_{\ell > m} C_{\ell m} \psi_{\ell m}^{\text{core}}(r) \]

The last two terms represent the core-valence correlation, while inner-core correlation was introduced by using an MCPF basis for the (3s3p) core states. The muffin-tin functions for the outer valence electron P(n) were expanded in the B-spline basis and the corresponding equations were solved under the condition that the wavefunctions vanish at the boundary. This scheme of non-orthogonal orbitals provides a flexible description for each LS term. The number of physical states we can generate in this method depends upon the size of the R-matrix box. Choosing \( a = 45 \text{ bohr} \) allows us to obtain a good description for all low-lying states of O− at the high-energy end but generated a set of pseudo-states, with the lowest states representing the remaining bound states and the rest representing the continuum. Table 1 compares our target energies with the experimental values. We also explored different target models (see Table 2), which differ by the amount of core-valence correlation incorporated.

Scattering models

In order to explore the dependence of the predicted photodetachment cross sections on the number of scattering channels and the polarization of the target, we used four scattering models with 3, 17, 34, and 60 target states. The largest close-coupling expansion included the 25 bound and autoionizing states of neutral oxygen derived from the 1s, 2s, 2p, and 3s configurations, plus a set of pseudo-states to account for the polarizability of the 2p6 3P0 ground state and the metastable 2p6 3D 1S target states. In each case the initial O− (2p6 3P0) state was calculated using the same close-coupling expansion.

Discussion of results

In the non-relativistic LS approximation used in the present work, the 2p photodetachment of O− (2p6 3P0) occurs in three partial waves, 52P, 52P, and 52D. The principal scattering channels are 2p(3P)/52P, 3S, and 52D.

Figures 1 and 2 compare the partial and total cross sections obtained with different target models. We see that correlation effects are extremely important in the present case. The low-correlated target models lead to spurious structures near the 2p thresholds. In this case, the (N=1)-electron system becomes correlated relative to the target description when we increase the number of scattering channels. The same effect is responsible for a huge spurious threshold spike of the calculated elastic cross section for the e−O collision problem [3].

A balanced description of the N-electron target and the (N-1)-electron scattering function is a common problem for close-coupling calculations in the near-threshold regime. For example, correlation effects in the ground state strongly affect the position and height of the (3p6 3P0) shape resonance in e−Mg collisions [4].

In contrast to common perception we did not find a noticeable dependence of the calculated photodetachment cross section on the degree to which the polarization of the target state was accounted for. This is illustrated in Figure 3, where partial cross sections in different scattering models are compared for the most correlated target model 3. Each scattering model differs by the number of scattering channels and by the polarization of the ground state accounted for. (The value given in parentheses should be compared with the experimental value of 5.23). Note that we found a stronger dependence of the photodetachment cross sections on the scattering model than the less-correlated target model 1 and model 2. This, however, is related to the problem of a balanced description of correlation in the N-electron target and the (N-1)-electron scattering functions discussed above, rather than to the polarization of the target states.

We also found a strong dependence of the photodetachment cross sections on the description of the initial O− (2p6 3P0) state. This is illustrated in Figure 4. The most stable results are obtained when the initial state is calculated with the close-coupling expansion that is also used for the scattering model.

Figure 5 compares our cross sections for 2p photodetachment to the available experimental and theoretical data. We note good agreement with experiment regarding the energy dependence of the cross section. Two step changes in the curves are due to an opening of new thresholds. Close agreement is also seen between the length (L) and velocity (V) forms of our predictions. However, our absolute numbers for the photodetachment cross sections exceed the experimental values [5,6] by about 40%. Although the measurements [5] were carried out 45 years ago, it is worth noting that these data are still being used to normalize relative data from current photodetachment experiments. Our previous calculations of B− and C− photodetachment [7] also showed excellent agreement with the experimental data regarding the energy dependence, but the absolute theoretical values exceeded the experimental cross sections by about 30%. Interestingly, both the B− and C− measurements for the photodetachment cross sections were normalized to the 0− data of [5]. The very similar differences obtained in three independent calculations with absolute experimental values based upon a single theoretical model suggests a possible systematic error of about 30% in [5].

References


Figures

Table 1. Comparison between the present ab initio and the observed (NIST Atomic Spectra Database) photo detachment excitation energies (in eV) of the physical oxygen states included in the close-coupling expansion.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Ab Initio</th>
<th>Experiment</th>
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<tbody>
<tr>
<td>0.0</td>
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<tr>
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<tr>
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Table 2. Properties of the 3P0 ground state of oxygen in different target models.

<table>
<thead>
<tr>
<th>Property</th>
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<th>Model 2</th>
<th>Model 3</th>
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</thead>
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<td>Energy (eV)</td>
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<td>-2.8521</td>
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<tr>
<td>Capitalization</td>
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</tr>
<tr>
<td>Polarization</td>
<td>0.017</td>
<td>-0.013</td>
<td>-0.013</td>
</tr>
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</table>

Figure 1: Partial-wave contributions to the photodetachment cross section for different target models (see Table 2), as a function of the photon energy. The solid line is the long-form and the dashed lines are the velocity-form results from the BSR-34 collision model.

Figure 2: Photodetachment cross section for different target models (see Table 2), as a function of the photon energy. The red dashed lines are the length-form partial-wave contributions from the BSR-34 collision model. The target thresholds are indicated by the vertical lines.

Figure 3: Partial-wave contributions to the photodetachment cross section for different collision models (see text) and target Model 3. The numbers in parentheses indicate the dipole polarization of the oxygen 2p6 3P0 ground state accounted for by the model. The experimental dipole polarization is 5.2 eV.

Figure 4: Photodetachment cross section for different models of the initial O− state, as obtained in the BSR-17 collision model and target Model 2. The solid and dashed lines represent the length and velocity results, respectively.

Figure 5: Photodetachment cross section from the present work, compared with other theoretical predictions and the available measurements. Note that the published experimental data were multiplied by 1.4.