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Junfang Gao

Jerry Peacher
Missouri University of Science and Technology, peacher@mst.edu

Don H. Madison
Missouri University of Science and Technology, madison@mst.edu

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Theoretical Treatment of Electron-Impact Ionization of Molecules

Junfang Gao, J.L. Peacher, and D.H. Madison

Department of Physics, University of Missouri-Rolla, Rolla, MO, USA 65409

Abstract. There is currently no reliable theory for calculating the fully differential cross section (FDCS) for low energy electron-impact ionization of molecules. All of the existing experimental FDCS data represent averages over all molecular orientations and this can be an important theoretical complication for calculations that are computer intensive. We have found that using an averaged molecular orbital is an accurate approximation for ionization of ground states. In this paper, we will describe the approximation, discuss its expected range of validity and show some FDCS results using the approximation for ionization of H_2 and N_2.

INTRODUCTION

Over the last two decades, there has been considerable interest in the fully differential cross section (FDCS) for electron-impact ionization of molecules. However most of this work has concentrated on either high incident electron energies or small molecules. For high enough energies, all the continuum electrons can be represented as plane waves and, in the plane wave impulse approximation (PWIA), the cross section becomes proportional to the momentum space wave function of the active electron. The PWIA was developed by McCarthy and his co-workers [1-4] and it has been extremely useful for studying molecular structure.

As the energy of the incident electron is decreased or the ejected electron has a low energy, it is clear that approximating the continuum electrons as plane waves will fail. Although there has been some improved theoretical models proposed for ionization of H_2 [5-6], very little work has been reported for ionization of larger molecules. One of the practical problems associated with any theoretical calculation of molecular ionization lies in the fact that existing experimental data represent an average over all molecular orientations and this can be a significant obstacle for approaches that are computer intensive. For example, we have introduced the 3DW (3 body distorted wave) model for charged particle ionization of atoms. This model contains the interactions between all two-particle subsystems to all orders of perturbation theory and practical calculations for a single point on a graph can take a day or more on the fastest computers. As a result, calculating enough points to take an accurate numerical 3-dimensional average becomes impractical (at least with the computing resources that we have available for use). Consequently, finding an alternative to brute force numerical averages is highly desirable.

In this paper, we report a simple approximation which eliminates the necessity for averaging cross sections over all molecular orientations. This approximation is to form an orientation averaged molecular orbital (OAMO) first and then use the averaged orbital for the calculation of the FDCS. We will demonstrate that this elementary approximation is valid for ionization of ground gerade states which are dominated by s-basis functions. Plane wave impulse approximation (PWIA) and distorted wave impulse approximation (DWIA) results will be presented for ionization of H_2 and N_2.

THEORY

We start with the plane wave impulse approximation (PWIA) which has been very successful for high energy collisions. In the PWIA, the FDCS is given by

$$\sigma^{PWIA}(\hat{\mathbf{R}}) = \frac{4}{(2\pi)^5} \frac{k_a k_b}{k_i} F(\mathbf{k}_i, \mathbf{k}_a, \mathbf{k}_b) \left| T(\hat{\mathbf{R}}) \right|^2 \tag{1}$$

where $(\mathbf{k}_i, \mathbf{k}_a, \mathbf{k}_b)$ are the momenta of the (incident, fast-final, slow-final) electrons, respectively. F is an elementary function of these momenta [4] and

$$T(\hat{\mathbf{R}}) = \int e^{i\mathbf{q}\bullet\mathbf{r}} \, \Phi(\mathbf{r},\mathbf{R}) \, d\mathbf{r} \tag{2}$$

Here $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_a - \mathbf{k}_b$ is the momentum transferred to the residual ion and $\Phi(\mathbf{r},\mathbf{R})$ is the molecular orbital (MO) which depends on the orientation of the molecule determined by the internuclear vector $\mathbf{R}$. To perform a proper average over orientations, one must average eq. (1) over all possible orientations.

$$\sigma^{PWIA} = \frac{1}{4\pi} \int \sigma^{PWIA}(\hat{\mathbf{R}}) \, d\hat{\mathbf{R}} \tag{3}$$

For the orientation averaged molecular orbital (OAMO) approximation which we have proposed, the orientated MO is replaced by

$$\phi^{OAMO}(\mathbf{r}) = \frac{1}{4\pi} \int \Phi(\mathbf{r},\mathbf{R}) \, d\hat{\mathbf{R}} \tag{4}$$

Now eq. (2) does not depend upon the orientation of the molecule

$$T^{OA} = \int e^{i\mathbf{q}\bullet\mathbf{r}} \, \phi^{OAMO}(\mathbf{r}) \, d\mathbf{r} \tag{5}$$

and the OA cross section is given by

$$\sigma^{PWIAOA} = \frac{4}{(2\pi)^5} \frac{k_a k_b}{k_i} F(\mathbf{k}_i, \mathbf{k}_a, \mathbf{k}_b) \left| T^{OA} \right|^2 \tag{6}$$

Using the OAMO for the calculation of the FDCS represents a significant simplification since: (1) the OAMO is relatively easy to calculate and (2) it only has to be calculated once since it is independent of the incident electron energy.

As a first attempt to improve the PWIA, we have proposed the distorted wave impulse approximation (DWIA). The idea of the DWIA is to take advantage of the factorization simplification of the PWIA and then to replace the plane waves in eq. (2) by distorted waves. As a result, the T-factor of eq. (2) becomes

$$T^{DWIA} = \int \chi_a^{-*}(\mathbf{k}_a,\mathbf{r}) \, \chi_b^{-*}(\mathbf{k}_b,\mathbf{r}) \, \chi_i^{+}(\mathbf{k}_i,\mathbf{r}) \, \phi^{OAMO}(\mathbf{r}) \, d\mathbf{r} \tag{7}$$

where (χ_i, χ_a, χ_b) are (incident, fast-final, slow-final) distorted waves, respectively. The distorted waves are calculated in the normal way as eigenfunctions of the Schrödinger equation using a spherically symmetric potential obtained from the charge density for the molecule averaged over all orientations. For the incident channel distorted wave, the charge density for a neutral molecule is used and for the final channel distorted waves, the charge density for a molecular ion is used. The DWIA cross sections are given by

$$\sigma^{DWIA} = \frac{4}{(2\pi)^5} \frac{k_a k_b}{k_i} F(\mathbf{k}_i, \mathbf{k}_a, \mathbf{k}_b) \left| T^{DWIA} \right|^2 \qquad (8)$$

RESULTS

The relative simplicity of the PWIA allows us to test the validity of using the OAMO approximation. If the approximation were valid, eqs. (3) and (6) should give identical results. We have investigated the validity of the approximation for ionization of H_2 and N_2. We have formed Hartree-Fock MO's for both molecules using the GAMES software [7]. For H_2, the ground state wave function was formed from three s-basis functions and for N_2, the ground state wave function was formed from two s-basis functions and one p-basis function.
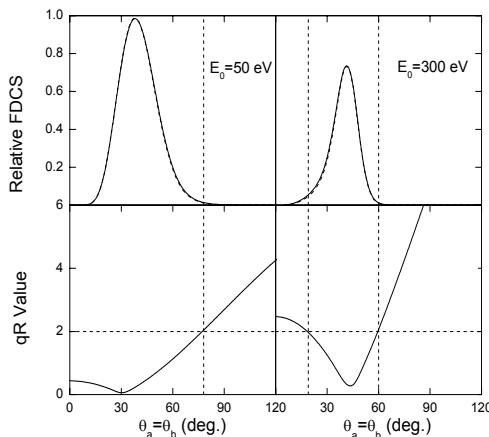

FIGURE 1. Upper part of the figure is the relative FDCS for electron impact ionization of H_2 in the coplanar symmetric scattering geometry. For coplanar symmetric scattering, the electrons are detected with equal energies and at equal angles on opposite sides of the beam direction. The energy of the incident electron is E_0 and each outgoing electron has an energy of $(E_0 - E_{ion})/2$ where E_{ion} is the ionization energy of the ground state orbital. The horizontal axis is the angular location for the two electron-detectors and the corresponding qR value is shown in the lower part of the figure where R=1.4 a_0.

In fig. 1, σ^{PWIA} and σ^{PWIAOA} results are compared for ionization of H_2 by 50 and 300 eV incident-energy electrons for coplanar symmetric scattering. Although it is hardly visible on the figure, there are actually two cross sections in the top part of the figure. It can be shown by analytical integration that, if a gerade state s-basis function

is used to calculate σ^{PWIA} and σ^{PWIAOA}, the results are the same providing qR (momentum transfer times internuclear distance) is less than about two. In the bottom half of fig. (1), the qR values corresponding to the scattering angles are shown and the vertical dashed line indicates where qR crosses two. It is seen that the cross sections are very small for $qR > 2$. However, the OAMO approximation is still valid even for $qR > 2$.
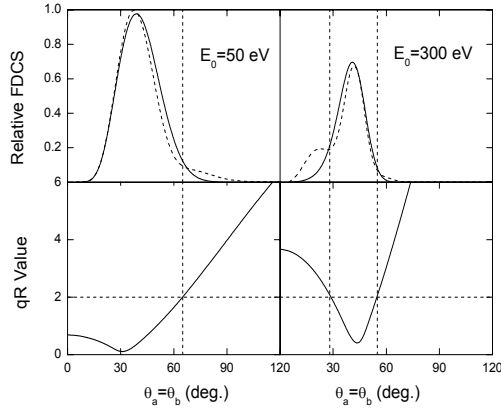

FIGURE 2. Same as Fig. 1 except for ionization of N_2 where R=2.1 a_0.

Figure 2 shows the same comparison for electron-impact ionization of N_2. Here we see that using the OAMO to calculate the OA cross sections is reliable for $qR < 2$ as expected. For $qR > 2$, the approximation is still reasonably good except for high energy and small scattering angles.
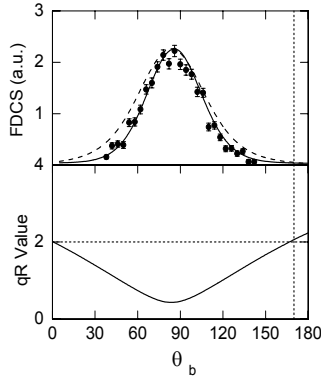

FIGURE 3. Upper part of the figure are the FDCS for electron-impact ionization of H_2 for coplanar asymmetric scattering. The energy of the incident electron is 4087 eV, the faster final state electron is observed at 3^0 and the energy of the ejected electron is 20 eV. The experimental data are those of Cherid *et al.* [8], the solid curve are the DWIA results; and dashed curve are PWIA results. The horizontal axis is the observation angle for the ejected electron and the corresponding qR value is shown in the lower part of the figure.
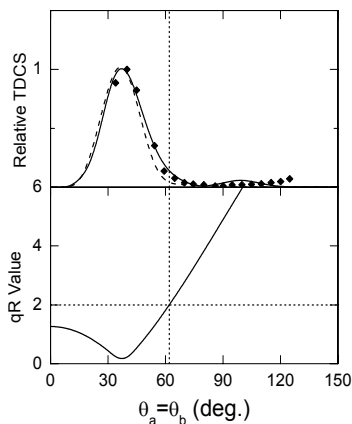
FIGURE 4. Upper part of the figure is the relative FDCS for electron-impact ionization of N_2 for coplanar symmetric scattering. The energy of the incident electron is 75.6 eV and both final state electrons have energy of 30 eV. The experimental data are those of Hussey and Murray [9], the solid curve are the DWIA results; and the dashed curve are PWIA results. The horizontal axis is the angular location for the two electron-detectors and the corresponding qR value is shown in the lower part of the figure.

Figures 3 and 4 compare experimental and theoretical results for ionization of H_2 and N_2. For H_2, experimental data are absolute and we have normalized our relative cross sections to experiment at the maximum value. It is seen that there is excellent agreement between experiment and the DWIA at this high energy (of course there is also little difference between the PWIA and DWIA at this energy). Figure 4 compares experiment and theory for low energy electron-impact ionization of N_2 for coplanar symmetric scattering. For this case, the PWIA does not predict a measurable cross section for larger angles. Although the large angle behavior does not agree with experiment, the DWIA, on the other hand, does predict a measurable large angle peak in the cross section. Large angle peaks in the FDCS are normally attributed to the atomic electron being back scattered from the ion. Since the physics contained in a distorted wave is elastic scattering from the molecule (initial state) and ion (final state), the fact that the DWIA contains a large angle peak while the PWIA does not clearly indicates that this peak results from elastic back scattering from the ion. The lack of good quantitative agreement for the largest angles may also be related the fact that qR is quite a bit larger than 2 in this angular region which means that using the OAMO to calculate orientation averaged FDCS becomes questionable.

CONCLUSIONS

In conclusion, we have shown that using orientation averaged molecular orbital (OAMO) to calculate the FDCS averaged over all molecular orientations is reliable for ionization of H_2 at all energies and all qR values where the cross section is large enough to be measured. For ionization of N_2, the approximation was valid for $qR < 2$

at all energies and also for $qR > 2$ except for small angles and high energies. This elementary approximation for evaluating orientation averaged cross sections will greatly simplify the evaluation of an orientation averaged FDCS for electron-impact ionization of molecules using better and more sophisticated theoretical approaches.

We also used the OAMO to calculate the DWIA FDCS for ionization of H_2 and N_2. We found that the DWIA represents an improvement over the PWIA particularly for low energies where the PWIA fails to predict the secondary large angle peaks. The DWIA was in qualitative, but not quantitative, agreement with the secondary large angle peak seen in the experimental data.

ACKNOWLEDGMENTS

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