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An Elementary Method for Calculating Orientation-Averaged Fully Differential Electron-Impact Ionization Cross Sections for Molecules

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An elementary method for calculating orientation-averaged fully differential electron-impact ionization cross sections for molecules

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Currently there are no reliable theoretical approaches for calculating fully differential cross sections (FDCS) for low-energy electron-impact ionization of large molecules. We have recently introduced the distorted-wave impulse approximation as a first step in developing improved theoretical approaches. One significant obstacle to evaluating improved theoretical approaches which require significant computer resources lies in the fact that the existing experimental data require taking averages over all molecular orientations. To circumvent this problem, it has been proposed to approximate the orientation-average by using an orientation-averaged molecular orbital in the calculation of the FDCS. The theoretical justification and expected range of validity for the approximation is given in this paper. Examples are presented for electron-impact ionization of H_2 and N_2. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2118607]

The investigation of fully differential cross sections (FDCS) for molecular ionization by electron impact, normally referred to as $(e, 2e)$, represents a powerful tool to study the electronic structure of molecules as well as to examine the fundamental interactions between continuum electrons and molecules. Over the last few decades, there have been many theoretical and experimental studies performed for the $(e, 2e)$ process with molecular targets. However most of these studies were primarily interested in molecular structure and most were for high incident energy or small molecules.[1–10] At high enough energies, where all the continuum electrons can be expressed as plane waves, the FDCS becomes proportional to the momentum space wave function so that measuring the cross section translates into a direct measurement of the active electron's wave function. A very successful theoretical approach for interpreting these high-energy data is the plane-wave impulse approximation (PWIA) of McCarthy and co-workers[1–4] and much valuable information about molecular wave functions was obtained from these studies. In order to investigate the collision dynamics for big molecules ionized by lower incident-energy electrons, better theoretical approaches are needed. All theoretical approaches for the FDCS for electron-impact ionization of molecules use the Born-Oppenheimer approximation to describe the target. As a result, only the electronic part of the molecular wave function is treated with the vibrational and rotational parts being neglected. Even with this major simplification of the problem, one still has to deal with the fact that almost all the existing experimental data represent an average over all molecular orientations except for some very recent $(e, 2e)$ measurements,[3] which were performed for the oriented molecules.[11,12] For elementary approaches, like the PWIA, these orientation averages can be performed analytically. For more complicated theoretical approaches, analytical averages are not possible and one must resort to numerical averages. However, if calculating the FDCS for a single fixed orientation requires significant computer resources, calculating the large number of different orientations required for an accurate numerical average can become impractical. Consequently, an alternative method to obtain orientation averages becomes highly desirable.

To perform a proper average over all orientations, one must evaluate the T matrix for a particular orientation, and then repeat this process for enough orientations to be able to perform an accurate average over all orientations. We recently introduced the idea of constructing an orientation-averaged molecular orbital (OAMO) which was then used in the distorted-wave impulse approximation (DWIA) to calculate the orientation-averaged FDCS for electron-impact ionization of N_2.[13] In this approach, the OAMO was generated first and then it was used in the T matrix. As a result, the T matrix is evaluated only once with a single OAMO instead of many times for many orientations. The purpose of this paper is to evaluate the conditions of validity for using OAMO wave functions to calculate orientation-averaged FDCS.

To investigate the conditions of validity for using OAMO wave functions in FDCS calculations, we will analytically evaluate the PWIA FDCS both with a proper orientation average and with an OAMO. The PWIA FDCS with a proper orientation average is given by[4]

$$\text{FDCS} = \frac{4}{(2\pi)^5} \frac{k_a k_b}{k_i} F(\mathbf{k}_i, \mathbf{k}_a, \mathbf{k}_b)\sigma, \tag{1}$$

where

$$\sigma = \frac{1}{4\pi} \int d\Omega_R \left| \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \psi_j(\mathbf{r}, \mathbf{R}) \right|^2. \tag{2}$$

In Eq. (1), $F(\mathbf{k}_i, \mathbf{k}_a, \mathbf{k}_b)$ is an elementary function of the momenta of the incident ($\mathbf{k}_i$), scattered ($\mathbf{k}_a$), and ejected electrons ($\mathbf{k}_b$), respectively, $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_a - \mathbf{k}_b$ is the momentum transferred to the residual ion, and $\psi_j(\mathbf{r}, \mathbf{R})$ is the molecular
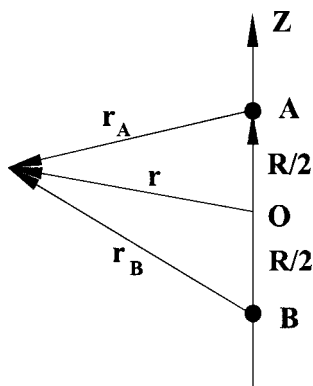
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FIG. 1. Coordinate system used for the LCAO for diatomic molecules. The origin is at the center of mass.

FIG. 2. Ratio of σ_g^{OA}/σ_g as a function of qR.

orbital for the active electron with $\mathbf{R}$ the internuclear vector. In the OAMO approximation, σ is replaced with

$$\sigma^{OA} = \left| \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \phi_j^{OA}(\mathbf{r}) \right|^2, \tag{3}$$

where

$$\phi_j^{OA}(\mathbf{r}) = \frac{1}{4\pi} \int \psi_j(\mathbf{r},\mathbf{R})\, d\Omega_R. \tag{4}$$

Here $\phi_j^{OA}(\mathbf{r})$ is the OAMO.

We will work in the framework of the linear combination of atomic orbital (LCAO) approach in which the molecular wave function is expressed as a sum of orbitals for each nucleus, and we will restrict our attention to diatomic molecules. Figure 1 shows the coordinate system we will be using with the z axis aligned along the internuclear axis and the origin at the center of mass.

In the LCAO approach, the MO is expressed in terms of a linear combination of s-basis states, p-basis states, etc. As will be shown below, using the OAMO in the calculation of the FDCS will be valid for gerade states if the MO's are dominated by the s-basis states. This can be seen as follows. For *gerade* states, the generic primitive s-basis function for a diatomic molecule has the form

$$\psi_g^{s\text{-basis}}(\mathbf{r},\mathbf{R}) = N\left[e^{-a(\mathbf{r}-\mathbf{R}/2)^2} + e^{-a(\mathbf{r}+\mathbf{R}/2)^2}\right], \tag{5}$$

where N and a are constants. If the wave function of Eq. (5) is used in Eq. (2), it can be shown that

$$\sigma_g = 2|A|^2\left[1 + \frac{\sin(qR)}{qR}\right]. \tag{6}$$

Similarly, if Eq. (5) is used to construct the OAMO of Eq. (4), the cross section of Eq. (3) is

$$\sigma_g^{OA} = \frac{8|A|^2}{(qR)^2}(1 - \cos(qR)). \tag{7}$$

If $qR \ll 1$, the σ_g of Eq. (6) reduces to

$$\sigma_g \to 4|A|^2 \tag{8}$$

and σ_g^{OA} of Eq. (7) for $qR \ll 1$ is

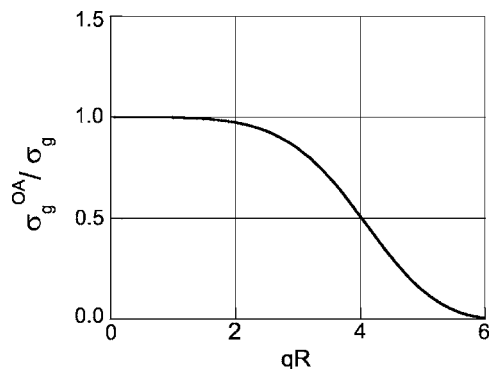$$\sigma_g^{OA} \to 4|A|^2. \tag{9}$$

Consequently, in the limit $qR \ll 1$ we have

$$\sigma_g = \sigma_g^{OA}. \tag{10}$$

To investigate the range of validity for Eq. (10), the ratio of σ_g^{OA}/σ_g is plotted in Fig. 2. As can be seen from the figure, $\sigma_g \approx \sigma_g^{OA}$ for $qR \lesssim 2$. Consequently the OAMO approximation is valid for a fairly broad range of qR values for a gerade state providing that the MO is dominated by the s-basis functions. As will be shown below, for the case of ionization of N_2 studied by Gao *et al.*,[13] the ground gerade state is dominated by the s-basis states and essentially all the measured experimental data has $qR \lesssim 2$ which explains the success of that work.

We now consider the ungerade MO in the LCAO approximation for diatomic molecules. The primitive s-basis states have the form

$$\psi_u^{s\text{-basis}} = N\left[e^{-a(\mathbf{r}-\mathbf{R}/2)^2} - e^{-a(\mathbf{r}+\mathbf{R}/2)^2}\right].$$

If this wave function is used for the proper orientation average, we find that Eq. (2) yields

$$\sigma_u = 2|A|^2\left[\frac{\sin(qR)}{(qR)} - 1\right]. \tag{11}$$

Similarly, the OAMO calculation for ungerade states yields

$$\sigma_u^{OA} = 0. \tag{12}$$

Again in the limit $qR \ll 1$ we have

$$\sigma_u \approx \sigma_u^{OA} = 0. \tag{13}$$

Of course, this is of academic interest only since this wave function would yield a zero cross section. Consequently, we conclude that the OAMO approximation is valid for gerade states dominated by s-basis states and small qR.

We now compare PWIA cross sections that have been properly averaged over all molecular orientations with PWIA cross sections calculated using the OAMO for H_2 and N_2. Due to its relatively simple structure, H_2 has often been investigated as a prototype for the theoretical treatment of electron-impact ionization of molecules.[5,8–10] Because the H_2 molecular orbital can be represented as a linear combination of s-primitive Gaussian functions, it is a good example to be used to investigate the validity of Eq. (10). We have used the
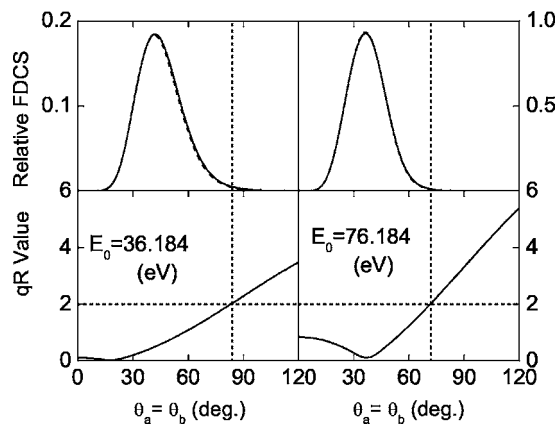
FIG. 3. Upper part of the figure is the relative FDCS for electron-impact ionization of H_2 in the coplanar symmetric scattering geometry. For coplanar symmetric scattering, the electrons are detected with equal energies and at equal angles on opposite sides of the beam direction. The energy of the incident electron E_0 is shown in each part of the figure 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. The solid lines are the PWIAOA results and the dashed lines are the PWIA results.

GAMES (Ref. 14) software program to obtain the orientation-dependent wave functions of Eq. (2) and the OAMO of Eq. (4). Figures 3 and 4 compare the PWIAOA in which the OAMO is used in the calculation with the PWIA in which the orientation-dependent orbital is used in the T-matrix calculation and then the average over orientations is performed analytically for coplanar symmetric electron-impact ionization of H_2. The upper part of the figure contains the cross sections as a function of the equal-angles for the two equal energy outgoing electrons and the bottom part of the figure contains the corresponding qR values.

Although it is not possible to see the difference in a journal figure, the top part of Figs. 3 and 4 actually contains two cross sections—the PWIAOA and the PWIA. The vertical dashed lines indicate the boundary for $qR=2$. It can be seen that the cross sections are very small for $qR>2$. Interestingly, we find no indication of a breakdown for the OAMO approximation even for $qR>2$. From the figures it is seen that the maximum in the cross section tends to occur near the minimum qR value particularly for the higher ener-
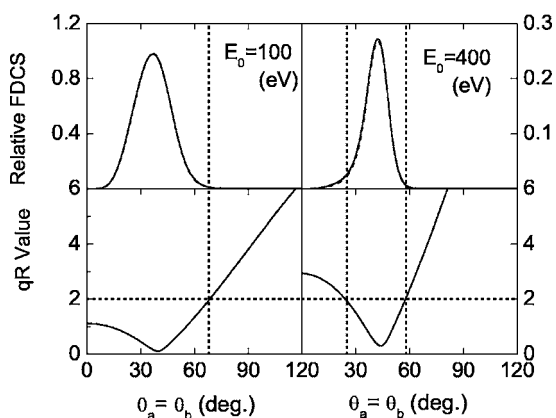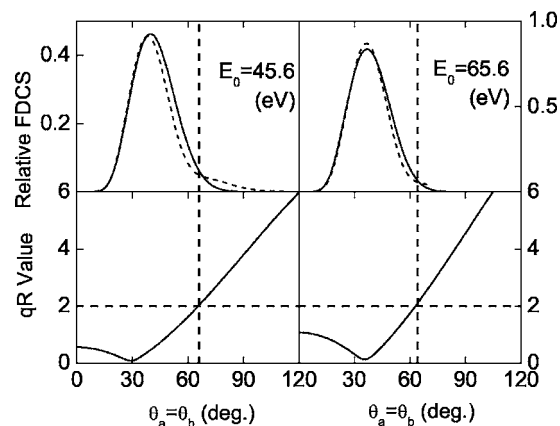
FIG. 5. Same as Fig. 3 except for electron-impact ionization of N_2.

gies. This is to be expected since the maximum in the cross section occurs near the angle that would be predicted for a binary collision between the projectile electron and an atomic electron at rest with the residual ion playing no role. As a result this peak is normally called the binary peak and the angular location comes closer to the classical prediction with increasing energy. Since q is the momentum of the residual ion, the minimum in qR corresponds to the smallest role for the residual ion and consequently the closest to a classical binary collision between the two electrons.

In Gao *et al.*,[13] the exact and PWIAOA cross sections were compared for ionization of the $3\sigma_g$ ground state of N_2 for coplanar symmetric scattering. Here we note that the $3\sigma_g$ orbital satisfies the criteria of dominance by s-state basis functions so we would expect that the PWIAOA calculation should be valid if $qR \leq 2$. In Figs. 5 and 6, the PWIA and PWIAOA results for N_2 are shown for a range of energies. The MO from GAMES were obtained using two s-basis states and one p-basis state. The small contribution from the p-basis state causes the small difference between the two results. Nevertheless, with the exception of 405.6 eV small scattering angles, the use of the OAMO for the calculation of orientation-averaged cross sections is very good even for $qR>2$. For an incident energy of 405.6 eV and small scattering angles, there is a significant difference between PWIA and PWIAOA for $qR>2$. On the other hand, this was the only significant difference between the two calculations that

FIG. 4. Same as Fig. 3 except for higher incident-electron energies.
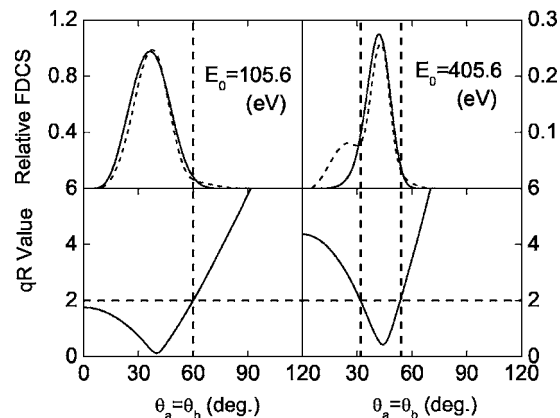
FIG. 6. Same as Fig. 5 except for higher incident-electron energies.

we found. It is interesting to note that PWIA consistently crosses from below the PWIAOA to above it as qR passes through 2. We are unsure if there is some significance for this observation.

In summary, Gao *et al.*[13] proposed the orientation-averaged MO idea for approximating the average over all molecular orientations in the calculation of the FDCS for electron-impact ionization of molecules. In this paper, we have shown the justification for this idea and have demonstrated that the approximation should be valid for calculating the ionization of gerade states providing the MO is dominated by s-basis functions and providing $qR \leq 2$. The validity of this replacement is further demonstrated by comparing exact and OAMO PWIA cross sections for ionization of H_2 and N_2. For ionization of H_2, there is so little difference between PWIA and PWIAOA that it cannot be seen in a journal figure for all qR values. For ionization of N_2, except for small angles and high energy, there is a small difference between the two calculations due to the p-basis-state contribution. However, the difference is small enough that the use of the OAMO represents an approximation which is acceptably accurate. This elementary approximation for evaluating orientation-averaged cross sections will greatly simplify the evaluation of orientation-averaged FDCS for electron-impact ionization of molecules using better and more sophisticated theoretical approaches. In a future work, we plan to use the OAMO to calculate distorted-wave Born approximation (DWBA) and molecular three-body distorted wave (M3DW) results for N_2 to compare with the experimental measurements of Refs. 15–17.

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