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Fully Differential Cross Sections for Low-Energy Electron-Impact Ionization of Nitrogen Molecules

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Fully differential cross sections for low-energy electron-impact ionization of nitrogen molecules

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Currently there is no accurate theoretical approach available for treating fully differential cross sections (FDCS) for low-energy electron-impact ionization of large molecules. For high incident energies, the plane wave impulse approximation (PWIA) generally yields good agreement with experimental data. In this paper, the distorted wave impulse approximation (DWIA) is used to calculate FDCS for low-energy electron-impact ionization of N_2. To perform the necessary average over all molecular orientations, we propose an orientation average (OA) approximation. Although the DWIA results represent an improvement over the PWIA for intermediate energies, an improved theory is necessary for lower energies. However, the OA approximation will greatly simplify the evaluation of improved theories for lower energies.

The measurement 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 interaction 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 for high incident-energy electron-impact ionization of molecules [1]. 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 [2,4]. Much valuable information about molecular wave functions were obtained from these studies.

Present theoretical approaches for the ionization of molecules have concentrated either on high incident energy or small molecules [1–10]. The purpose of this paper is to propose a distorted wave impulse approximation (DWIA) coupled with an orientation average (OA) approximation that could be used for the theoretical treatment of low-energy electron-impact ionization of heavier molecules. As a first example, we apply it to calculate the FDCS for coplanar symmetric ionization of N_2.

For a description of the proposed DWIA, we start with the FDCS given by the PWIA [4] in which the Born-Oppenheimer approximation is used to treat the rotational, vibrational, and electronic parts of the wave function. The initial vibrational state is assumed to be the lowest one and the initial rotational states are normalized to unity by Maxwellian weight factors. The final rotational and vibrational states are also assumed to be degenerate and obey the closure relations. With these assumptions, the PWIA FDCS is given by

$$\frac{d^7\sigma}{d\Omega_a d\Omega_b dE_b d\Omega_R} = \frac{4}{(2\pi)^5}\frac{k_a k_b}{k_i}F(\vec{k}_i,\vec{k}_a,\vec{k}_b)\sigma^{PWIA}(\mathbf{R}), \quad (1)$$

where

$$\sigma^{PWIA}(\mathbf{R}) = \left| \int d\mathbf{r}\beta_a^*(\vec{k}_a,\mathbf{r})\beta_b^*(\vec{k}_b,\mathbf{r})\beta_i(\vec{k}_i,\mathbf{r})\psi_j(\mathbf{r},\mathbf{R}) \right|^2. \quad (2)$$

In Eqs. (1) and (2), $F(\vec{k}_i,\vec{k}_a,\vec{k}_b)$ is an elementary function of the momenta of the incident $(\vec{k}_i)$, scattered $(\vec{k}_a)$, and ejected electrons $(\vec{k}_b)$ [4]. The functions $\beta_i(\vec{k}_i,\mathbf{r})$, $\beta_a(\vec{k}_a,\mathbf{r})$, and $\beta_b(\vec{k}_b,\mathbf{r})$ are plane waves for the incident, scattered, and ejected electrons, and $\psi_j(\mathbf{r},\mathbf{R})$ is the molecular orbital for the active electron with $\mathbf{R}$ the internuclear vector.

Although the PWIA was enormously successful for high incident energies, it will fail for lower energies where plane waves are clearly inappropriate. The typical FDCS has a binary peak and a recoil peak and as the energy of the incident projectile decreases, the recoil peak becomes increasingly important. Because it is a binary approximation, the PWIA is able to predict the binary peak but not the recoil peak. The physical picture of the recoil peak is a double scattering in which the projectile has a binary collision with the atomic electron and then the atomic electron elastically scatters from the ion to the backward direction. The physics of elastic scattering from the ion is contained in distorted waves, and, for the case of atomic ionization, changing from plane waves to distorted waves greatly improved the agreement between experiment and theory for the recoil peak. Consequently we propose the DWIA in which the plane waves of Eq. (2) are replaced by molecular distorted waves,

$$\sigma^{DWIA}(\mathbf{R}) = \left| \int d\mathbf{r}\chi_a^{-*}(\vec{k}_a,\mathbf{r})\chi_b^{-*}(\vec{k}_b,\mathbf{r})\chi_i^{+}(\vec{k}_i,\mathbf{r})\psi_j(\mathbf{r},\mathbf{R}) \right|^2, \quad (3)$$

where $\chi_i(\vec{k}_i,\mathbf{r})$, $\chi_a(\vec{k}_a,\mathbf{r})$ and $\chi_b(\vec{k}_b,\mathbf{r})$ are the molecular distorted waves for the incident, fast-final, and slow-ejected electrons. The molecular distorted waves are calculated using a spherically averaged static potential for the molecule U_S, a polarization potential U_P, and a local exchange potential U_E. Consequently, the Schrödinger equation for the incident channel distorted wave is given by

$$\left(T + U_S + U_P + U_E - \frac{k_i^2}{2}\right)\chi_i^-(\vec{k}_i, \mathbf{r}) = 0, \tag{4}$$

where T is the kinetic energy operator. The static potential U_S is obtained from the charge distribution $\rho(\mathbf{r}, \mathbf{R})$ for N_2.

$$U_S(r) = V_{nuc}(r) + V_{ele}(r), \tag{5}$$

where

$$V_{ele}(r) = \left\langle\left\langle \int \frac{\rho(\mathbf{r}', \mathbf{R})d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \right\rangle\right\rangle, \tag{6}$$

$$\rho(\mathbf{r}, \mathbf{R}) = \sum_{i=1}^{N} n_i|\psi_i(\mathbf{r}, \mathbf{R})|^2, \tag{7}$$

where N is the number of molecular orbitals, n_i is the number of electrons in each orbital, and $\psi_i(\mathbf{r}, \mathbf{R})$ is the Hartree-Fock molecular orbital obtained from GAMESS [11]. The double brackets in Eq. (6) indicate taking a spherical average over all orientations of both $\mathbf{r}$ and $\mathbf{R}$. A spherical average is also taken for the nuclear potential $V_{nuc}(r)$. In this calculation, we also include a phenomenological polarization potential in our distorted wave calculation.

$$U_P(r) = -\frac{\alpha_0}{2r^4}\left\{1 - \exp\left[-\left(\frac{r}{a}\right)^4\right]\right\}, \tag{8}$$

where the α_0 is the dipole polarizability, and a is an adjustable parameter that acts as a cutoff radius for the polarization potential. The dipole polarizability α_0 is 11.744 in atomic units for N_2 [12]. There have been several studies using this form of the polarization potential for elastic scattering of electrons from nitrogen molecules, and various cutoff parameters have been used ranging from $1.6a_0$ [13] to $2.3a_0$ [14,15]. However simply using one of these cutoff values is not likely to accurately approximate the effects of polarization for two reasons: (1) These results are for neutral nitrogen, whereas our two final state distorted waves are calculated for scattering from a nitrogen ion for which polarization effects will be different. (2) Using a single cutoff parameter would correspond to using an energy independent potential, whereas a proper polarization potential should be energy dependent [16,17]. Having no further guidance on how to pick the parameter, we decided to take the easiest approach, which was to use the same polarization potential for both the initial and final channels and pick the cutoff parameter to give the best fit to the experimental binary peak. The values of a we found are 2.15, 1.8, 1.5, 1.3, 0.98, 0.85 a.u. for 35.6, 55.6, 75.6, 100, 200, 400 eV incident electron energies, respectively. Although we do not like adjustable parameters, we think these values are sensible for the following reason. Rice et al. [18] found that the cutoff parameter should be about the same size as the target charge cloud in their study of the polarization potential for electron-impact excitation of helium. In our case, the size of the charge distribution is about $2a_0$, so our values are in line with this expectation. Finally, it should be noted that all of the previous works for neutral nitrogen used a power of 6 in the exponent instead of the power of 4 we used. However, we

found that the results were not very sensitive to the power in the exponent.

For the exchange potential, we use the local approximation of Furness and McCarthy [19],

$$U_E = \frac{1}{2}\{(k_i^2 - U_s) - \sqrt{(k_i^2 - U_s)^2 + 2\rho_s(r)}\}. \tag{9}$$

Here $\rho_s(r)$ is the orientation and angle average of the molecular electronic charge density,

$$\rho_s(r) = \langle\langle\rho(\mathbf{r}, \mathbf{R})\rangle\rangle.$$

The radial charge density is defined such that the integral over r yields the number of electrons in the molecule. The two final channel distorted waves are obtained from a Schrödinger equation similar to (4),

$$\left(T + U_I + U_P + U_E - \frac{k_{a(b)}^2}{2}\right)\chi_{a(b)}^+(\vec{k}_{a(b)}, \mathbf{r}) = 0. \tag{10}$$

Here U_I is the spherically averaged static distorting potential for the ion obtained the same way as U_S except that the active electron is removed from the charge distribution. Following the procedure used for atomic ionization [20–22], we use the same U_P and U_E with appropriate energies for both the initial and final channels.

Although some preliminary results have been reported for the ionization of molecules with fixed orientations, the existing FDCS data for N_2 does not distinguish between different molecular orientations. Consequently, we must average the FDCS of Eq. (3) over all orientations. In principle, one could numerically average over all possible molecular orientations. However, our long-term objective is to develop the standard distorted wave Born approximation (DWBA) as well as the three-body distorted wave (3DW) [22] for molecules. For these calculations, it is impractical to consider performing a numerical average over orientations with present computing resources. As a result, we investigated various approximations for taking the average and found that a good approximation was to replace the orientated molecular wave function in Eq. (3) with a molecular wave function averaged over all orientations This type of averaging is in the spirit of the distorted wave approximation and we will call this the DWIAOA where OA stands for orientation average,

$$\sigma^{DWIAOA} = \left|\int d\mathbf{r}\chi_a^{-*}(\vec{k}_a, \mathbf{r})\chi_b^{-*}(\vec{k}_b, \mathbf{r})\chi_i^+(\vec{k}_i, \mathbf{r})\phi_j(\mathbf{r})\right|^2, \tag{11}$$

where

$$\phi_j^{OA}(\mathbf{r}) = \langle\psi_j(\mathbf{r}, \mathbf{R})\rangle. \tag{12}$$

Here the single bracket stands for averaging over all molecular orientations.

We first examine the accuracy of our orientation average DWIAOA by comparing it with McCarthy's PWIA. In the PWIA, the orientation average is performed analytically in momentum space [4] and McCarthy has generously given us his PWIA computer code. If we replace $\chi_i(\vec{k}_i, \mathbf{r})$, $\chi_a(\vec{k}_a, \mathbf{r})$, and $\chi_b(\vec{k}_b, \mathbf{r})$ in Eq. (11) by numerical plane waves, the re-
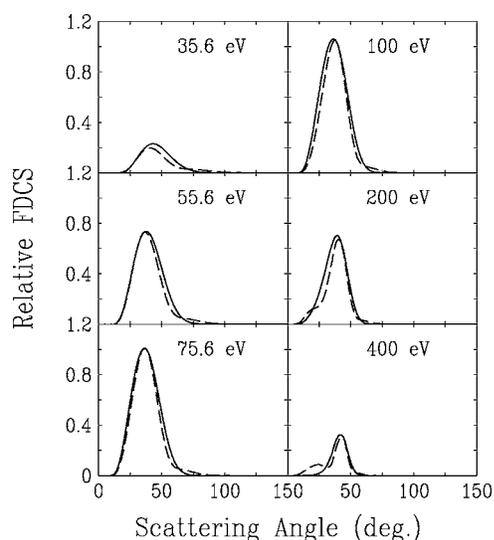
FIG. 1. Relative FDCS for electron-impact ionization of the $3\sigma_g$ state of N_2. The energy of the incident electron is noted in each part of the figure and the two final state electrons have equal energies. The theoretical curves are: dashed: PWIA; solid: PWIAOA. The theories have been normalized to unity at the 75.6 eV binary peak.

FIG. 2. Relative coplanar symmetric FDCS for electron-impact ionization of the $3\sigma_g$ state of N_2. The energy of the incident electron is noted in each part of the figure and the two final state electrons have equal energies. The experimental data are: solid circles: Hussey and Murray [23]; solid squares: Rioual *et al.* [24]. The theoretical curves are: dashed: PWIA; and solid: present DWIAOA. The cross sections have been normalized to unity at the angle where the experiment is maximum (except for 35.6 eV where the normalization is at 45°).

sulting PWIAOA would be the PWIA calculated within our orientation average approximation. Comparing PWIA and PWIAOA then represents a direct check of the accuracy of our approximation. Please note that this also represents a stringent test of our computer code since McCarthy's PWIA calculation is performed in momentum space with an analytical orientation average while our calculation is performed in coordinate space with our orientation averaged molecular orbital.

Figure 1 compares PWIA and PWIAOA results for ionization of the $3\sigma_g$ state of N_2. All calculations are performed in the coplanar symmetric scattering geometry. The incident projectile energy is noted in the figure; each of the two outgoing electrons will have an energy of $(E_0 - 15.6 \text{ eV})/2$. It is seen that there is little difference between the PWIA and PWIAOA for incident electron energies between 35 and 400 eV, which demonstrates the accuracy of our average orbital approximation. Interestingly, the largest difference between the two calculations is found for the lowest and highest energies.

Figure 2 compares the theoretical and experimental relative FDCS averaged over all molecular orientations for electron impact ionization of the $3\sigma_g$ state of N_2 in the coplanar symmetric geometry. The incident electron energy (E_i) is shown in each part of the figure and each outgoing electron's energy is $(E_i - 15.6 \text{ eV})/2$. The lower energy experimental results are those of Hussey and Murray [23] and the higher energy experimental data are those of Rioual *et al.* [24]. Each figure contains the PWIA results of McCarthy and the present DWIAOA results. The main features of the coplanar symmetric FDCS is the binary peak near 40° and, for lower energies, a much smaller secondary peak at larger angles. It is seen from Fig. 2 that both the PWIA and DWIAOA tend to predict the same location for the binary peak that is typically in relatively good agreement with experiment. The 200
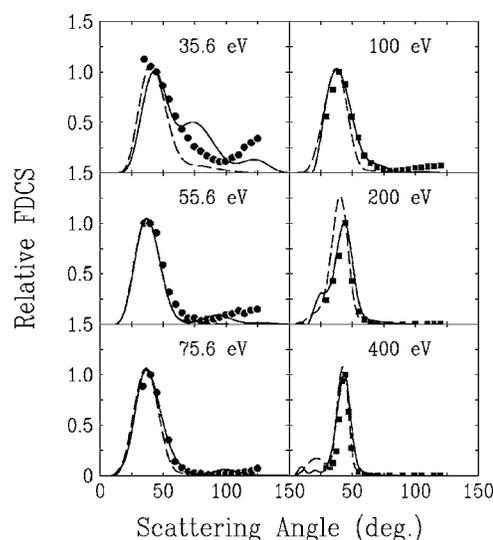
eV case of Fig. 2 is particularly interesting since the DWIAOA and PWIA have different locations for the binary peak and the DWIA is in better agreement with the data. Overall, the DWIAOA is in reasonable agreement with experiment for intermediate and high energies, with the agreement deteriorating as the energy becomes lower. To our knowledge, there are no other theoretical calculations available for comparison.

As we anticipated, the DWIAOA predicts a secondary peak for large angles and low energies while the PWIA does not. For the present case, this peak starts to become significant for energies less than about 100 eV. In Fig. 3, we show the 55.6 and 75.6 eV results on a semi logarithmic plot that allows one to see the secondary peak better. From the figure, it is seen that the experimental maximum for the secondary peak appears to be beyond the range of measurements while the DWIAOA predicts a peak maximum within the range of measurement. Recall that part of the motivation for trying the DWIA approach was to see if the secondary peaks would be predicted. From these results we see that the distorted waves do produce a secondary peak that clearly demonstrates
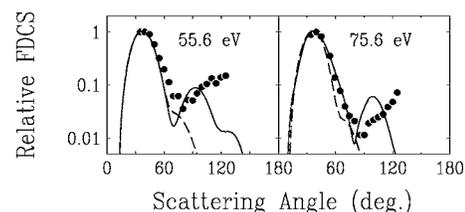

FIG. 3. Semilogarithmic plot for 55.6 and 75.6 eV. Otherwise it is same as Fig. 2.

that these peaks result from the interactions between the electron and molecule.

In summary, we have presented the DWIAOA theory for ionization of molecules and have applied the theory to electron-impact ionization of N_2 for coplanar symmetric scattering. We found that our orientation average wavefunction approximation was accurate for ionization of the ground gerade state. The DWIAOA was in better agreement with experiment than the PWIA, particularly for intermediate energies. Although the DWIAOA did predict a secondary peak, agreement with experiment was only qualitative. Another shortcoming of the present DWIA approach is the use of a polarization potential with adjustable parameters. Consequently, it would appear that a better theory

such as the DWBA or 3DW [22] will be required to achieve a more detailed understanding of the secondary peaks and low-energy scattering. The most important aspect of this paper is that it establishes the accuracy of the OA method, which greatly simplifies the calculation of these cross sections and makes approaches such as the DWBA or 3DW possible

[1] E. Weigold and I. E. McCarthy, *Electron Momentum Spectroscopy* (Kluwer Academic, Dordrecht/Plenum Publishers, New York, 1999).

[2] I. E. McCarthy and E. Weigold, Phys. Rep., Phys. Lett. **27**, 275 (1976).

[3] I. E. McCarthy and A. M. Rossi, Phys. Rev. A **49**, 4645 (1994).

[4] I. E. McCarthy and E. Weigold, Rep. Prog. Phys. **51**, 299 (1988).

[5] F. Robicheaux, J. Phys. B **29**, 779 (1996).

[6] H. Deutch and K. Becker, J. Phys. Chem. A **102**, 8819 (1998).

[7] C. Champion, J. Hanssen, and P. A. Hervieux, Phys. Rev. A **63**, 052720 (2001).

[8] A. L. Monzani, L. E. Machado, M. T. Lee, and A. M. Machado, Phys. Rev. A **60**, R21 (1999).

[9] P. Weck, O. A. Fojón, J. Hanssen, B. Joulakian, and R. D. Rivarola, Phys. Rev. A **63**, 042709 (2001).

[10] C. R. Stia, O. A. Fojón, P. F. Weck, J. Hanssen, B. Joulakian, and R. D. Rivarola, Phys. Rev. A **66**, 052709 (2002).

[11] M. W. Schmidt, K. K. Baldridge, J. A. Boats, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Mont-

gomery Jr., J. Comput. Chem. **14**, 1347 (1993).

[12] H. Feng, W. Sun, and M. A. Morrison, Phys. Rev. A **68**, 062709 (2003).

[13] P. G. Burke and N. Chandra, J. Phys. B **5**, 1696–1711 (1970).

[14] B. D. Buckley and P. G. Burke, J. Phys. B **10**, 725 (1977).

[15] M. A. Morrison and L. A. Collins, Phys. Rev. A **17**, 918 (1978).

[16] K. Onda and D. G. Truhlar, Phys. Rev. A **22**, 86 (1980).

[17] D. Thirumalai and D. G. Truhlar, Phys. Rev. A **26**, 793 (1982).

[18] J. M. Rice, D. G. Truhlar, D. C. Cartwright, and S. Trajmar, Phys. Rev. A **5**, 762 (1972).

[19] J. B. Furness and I. E. McCarthy, J. Phys. B **6**, 2280 (1973).

[20] D. A. Biava, H. P. Saha, E. Engel, R. M. Dreizler, R. P. McEachran, M. A. Haynes, B. Lohmann, C. T. Whelan, and D. H. Madison, J. Phys. B **35**, 293 (2002).

[21] D. A. Biava, K. Bartschat, H. P. Saha, and D. H. Madison, J. Phys. B **35**, 5121 (2002).

[22] A. Prideaux, D. H. Madison, and K. Bartschat (unpublished).

[23] M. J. Hussey and A. Murray, J. Phys. B **35**, 3399 (2002).

[24] S. Rioual, G. N. Vien, and A. Pochat, Phys. Rev. A **54**, 4968 (1996).