

# Low-energy electron scattering by N<sub>2</sub>O

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## Abstract

We present elastic integral, differential and momentum transfer cross sections for electron collisions with N<sub>2</sub>O. We show that, with a slight modification of a method of incorporating polarization effects proposed recently by us [Winstead, McKoy and Bettega, *Phys. Rev. A* **72**, 042721 (2005)] along with a flexible one-particle basis set, we can reproduce features in the experimental data that were not reproduced by earlier calculations. We also find evidence of a Ramsauer–Townsend minimum, which our calculation places at about 0.2 eV.

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## I. INTRODUCTION

Collisions of low-energy electrons with  $\text{N}_2\text{O}$  have been studied by numerous experimental and theoretical groups [1–14] in the past two decades. Earlier work [15–21] indicated the existence of two shape resonances in the low-energy cross section: one belonging to  $\Pi$  symmetry located around 2.4 eV, the other to  $\Sigma$  symmetry and located around 8 eV. Most of the recent calculations agree moderately well on these two features. There is also agreement between the calculated and measured elastic differential cross sections (DCSs) for energies of about 10 eV and above, even when polarization effects are omitted [10, 11], while disagreement between the calculated and measured DCSs at or near the resonances can be attributed to the fixed-nuclei approximation. However, even for energies between  $\sim 3$  eV and  $\sim 7$  eV (i.e., between the two shape resonances), serious discrepancies are found between theory and experiment for scattering angles smaller than  $60^\circ$ . Kitajima and coworkers [12] emphasized that the minimum seen in the experimental DCSs at these energies had not been reproduced by any calculations. They also noted that similar features, which theory likewise failed to reproduce, were seen in many other molecules.

Three of the recent theoretical calculations incorporated polarization effects, namely, the  $R$ -matrix calculations of Sarpal and coworkers [7] and of Morgan and coworkers [9] and the calculations of Winstead and McKoy [10] using the Schwinger multichannel (SMC) method. Only the last two reported DCSs. Although these calculations used different treatments of polarization, they give fairly consistent results for the integral cross section below 10 eV, with the exception that the calculations of Morgan and coworkers show no  $\Sigma$  resonance there. It is therefore both surprising and a challenge to theory that they do not, as mentioned above, reproduce the measured DCSs at nonresonant energies, especially since *all* of the experimental DCSs [4–6, 12] agree with each other; in particular, Kitajima and coworkers [12] report DCSs obtained from two independent measurements on different apparatuses that agree very well.

Our main purpose in the present paper is to explore what further steps are needed to bring calculated DCSs between  $\sim 3$  eV and  $\sim 7$  eV into agreement with experiment for  $\text{N}_2\text{O}$ , especially at scattering angles below  $60^\circ$ . In so doing, we also hope to provide good-quality calculated cross sections for low-energy electron scattering by  $\text{N}_2\text{O}$ . This work is a continuation of our earlier work on  $e^-$ - $\text{C}_2\text{H}_4$  collisions [23], where we addressed a similar

feature in the cross section [22], and it employs similar techniques, with some slight variations that will be described below.

The next section discusses our computational procedure, with emphasis on the treatment of polarization effects and the construction of the one-electron basis set. This is followed by a presentation and discussion of our results and a brief conclusion.

## II. COMPUTATIONAL PROCEDURES

Our scattering calculations were performed with the Schwinger Multichannel [24] method implemented for parallel computers [25, 26]. General features of the SMC method can be found in the references cited. Here we are interested in the representation of polarization and other details specific to the present calculations.

In the SMC method, the direct configuration space, describing a free electron and unperturbed molecular charge density, is constructed as follows:

$$\{\chi_i\} = \{\mathcal{A}(\Phi_1 \otimes \varphi_i)\} \quad (1)$$

where  $\Phi_1$  is the  $N$ -electron Hartree–Fock wave function for the target ground state,  $\varphi_i$  is a one-electron function unoccupied in  $\Phi_1$  (a virtual orbital), and  $\mathcal{A}$  is the antisymmetrizer. Polarization effects are taken into account by enlarging the configuration space to include configuration state functions (CSFs) of the type:

$$\{\chi_{ju}\} = \{\mathcal{A}(\Phi_j \otimes \varphi_u)\}; j \geq 2 \quad (2)$$

where  $\Phi_j$  are  $N$ -electron configurations that are singly excited (from a “hole” orbital into a “particle” orbital) relative to  $\Phi_1$ , and the  $\varphi_u$  are again one-electron functions chosen from the virtual-orbital space. The efficient choice of hole, particle, and scattering orbitals is a critical issue in practice and will be discussed next.

In our recent study of electron collisions with  $\text{C}_2\text{H}_4$  [23], we noted the advantages of modified virtual orbitals (MVOs) as particle orbitals. MVOs are generated by the diagonalization, in the virtual-orbital space, of a closed-shell cation Fock operator formed by removing electrons from  $\Phi_1$  [30]. They therefore retain the desirable orthogonality properties of the Hartree–Fock virtual orbitals but are ordered in such a way that the lowest-energy MVOs are compact and valence-like. This ordering provides a natural scheme for systematically

improving the representation of polarization. In seven of the eight irreducible representations of  $C_2H_4$ , we used the lowest 30 MVOs as particle orbitals and all six valence occupied orbitals as hole orbitals to form singlet-coupled states  $\Phi_j$ . In the strongly shape-resonant  $B_{2g}$  symmetry, we used only the first MVO as a particle orbital to form all singlet- or triplet-coupled excitations from the valence orbitals. Our purpose was to avoid over-correlation of the  $B_{2g}$  resonance that might place it too low in energy.

In the present study of  $N_2O$ , we found it necessary to modify slightly the procedure described above. Instead of using different approaches to resonant and nonresonant symmetries, we use the *same* approach for *each* symmetry: namely, that used for the nonresonant or weakly resonant symmetries of  $C_2H_4$ . We believe that the key difference between the two molecules is the lower effective symmetry of  $N_2O$ . Because we work with Cartesian Gaussian orbitals and  $N_2O$  lacks an inversion center, its effective symmetry is  $C_{2v}$ , in contrast to the  $D_{2h}$  symmetry of  $C_2H_4$ . In particular, the  $B_1$  and  $B_2$  representations contain, for  $N_2O$ , contributions that would separate, in a more symmetric molecule such as  $CO_2$ , into resonant  $\Pi_g$  and nonresonant  $\Pi_u$  components. Trial of different configuration-selection schemes indicated that including a sufficient representation of nonresonant polarization in  $B_1$  and  $B_2$  was a more important consideration than was avoiding over-correlation of the  ${}^2\Pi$  resonance.

The calculations were performed with the nuclei fixed at their ground-state equilibrium geometry, as in previous work [10]. To construct the target ground state and the set of MVOs, we used the package GAMESS [27] and its TZV+G(3d) basis set. We worked in the  $C_{2v}$  subgroup of the full  $C_{\infty v}$  group. The MVOs were generated by diagonalizing a +4 cationic Fock operator. In each representation of  $C_{2v}$ , our hole-particle space included all singlet excitations from the 8 valence occupied orbitals into the lowest 30 MVOs.

In  $C_2H_4$ , we found that adding basis functions on a grid of extra centers noticeably improved the description of forward scattering but was not critical to obtaining the minimum in the small-angle DCS. Such extra centers are more important in  $N_2O$ , possibly because the basis functions located on the H atoms in  $C_2H_4$  already bring in some longer-range and higher partial-wave contributions that are absent in an ordinary  $N_2O$  basis set. In particular, since  $N_2O$  is linear and the TZV+G(3d) basis set contains only  $s$ -,  $p$ -, and  $d$ -type functions, it only includes partial waves with azimuthal quantum numbers up to  $m = 2$ . We tested the importance of higher azimuthal quantum numbers by performing three calculations differing in their use of additional Cartesian Gaussian functions placed on extra (chargeless) centers

TABLE I: Number of Cartesian Gaussian functions (NCGF) and number of configuration state functions (NCSF) used in the scattering calculations (see text for discussion).

Symmetry	No extra centers		24 extra centers		44 extra centers	
	NCGF	NCSF	NCGF	NCSF	NCGF	NCSF
A <sub>1</sub>	108	12162	204	11602	284	14995
B <sub>1</sub>	108	9199	204	10821	284	14468
B <sub>2</sub>	108	9199	204	10685	284	13798
A <sub>2</sub>	108	4985	204	9925	284	13292

with locations chosen to produce  $m = 3$  partial-wave contributions while retaining  $C_{2v}$  symmetry. The first calculation used no extra centers, while in the second, 24 extra centers were added at the vertices of four hexagons with sides equal to 1.1 Å that were placed in planes perpendicular to the internuclear axis and halfway between or half a bond length beyond the nuclei. In the third calculation, we further included 18 centers located at the vertices of three larger hexagons (sides equal to 2.2 Å) centered on the nuclei, plus two extra centers located on the molecular axis but beyond the N and O atoms by distances equal to the N–N and N–O bond lengths, respectively. At each extra center, we placed one  $s$ -type Gaussian function with exponent 0.144 and one  $p$ -type function with exponent 0.2. Table I shows the number of Cartesian Gaussian functions and the number of CSFs employed in each calculation.

N<sub>2</sub>O has a small permanent dipole moment of 0.161 Debye [28]. Our calculated value, obtained with the larger basis set described above, is 0.618 Debye. We did not include an explicit correction for long-range, dipolar scattering. Because the calculated dipole is larger than the experimental value, including the dipole interaction through the usual closure procedure [29] would probably make the results worse rather than better, and at any rate, the correction would only be significant at very low energies or extreme forward angles. Besides, the extra centers should bring in dipole scattering up to a fairly high angular momentum (i.e., a fairly large impact parameter). We note that, although the partial-wave expansion of the elastic scattering amplitude for a fixed dipole is formally divergent at all angles, no special measures are needed to obtain finite results, both because we compute the amplitude

in the plane-wave representation and because we use a square-integrable representation of the wavefunction, which effectively discards the (unphysical) contribution from scattering at arbitrarily large impact parameters that leads to divergence when rotation is neglected.

### III. RESULTS AND DISCUSSION

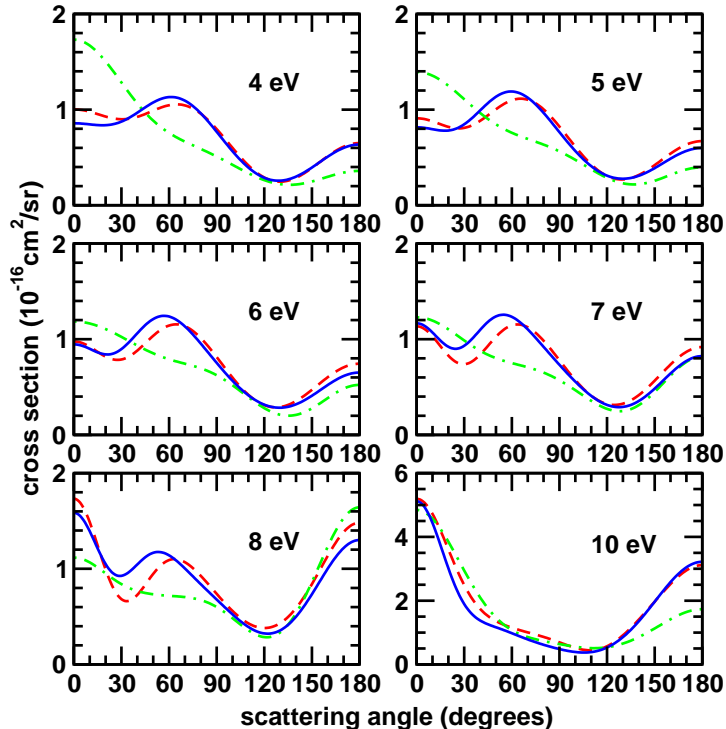


FIG. 1: (Color online) Differential cross sections for  $\text{N}_2\text{O}$  at 4, 5, 6, 7, 8 and 10 eV. Dot-dashed line (green), our results with no extra centers; dashed line (red), our results with 24 extra centers; solid line (blue), our results with 44 extra centers.

In Fig. 1 we compare our calculated DCSs at 4, 5, 6, 7, 8, and 10 eV obtained in the three different calculations described above. The inclusion of extra centers that can represent partial waves up to  $m = 3$  is clearly crucial for describing the minimum in the DCSs below  $60^\circ$ . However, Fig. 1 also shows that increasing the number of centers from 24 to 44 did not make a significant difference in the results. Although not shown, the integral and momentum transfer cross sections obtained in these different calculations were in close agreement. From here on, we will show only what we consider our best results, namely those

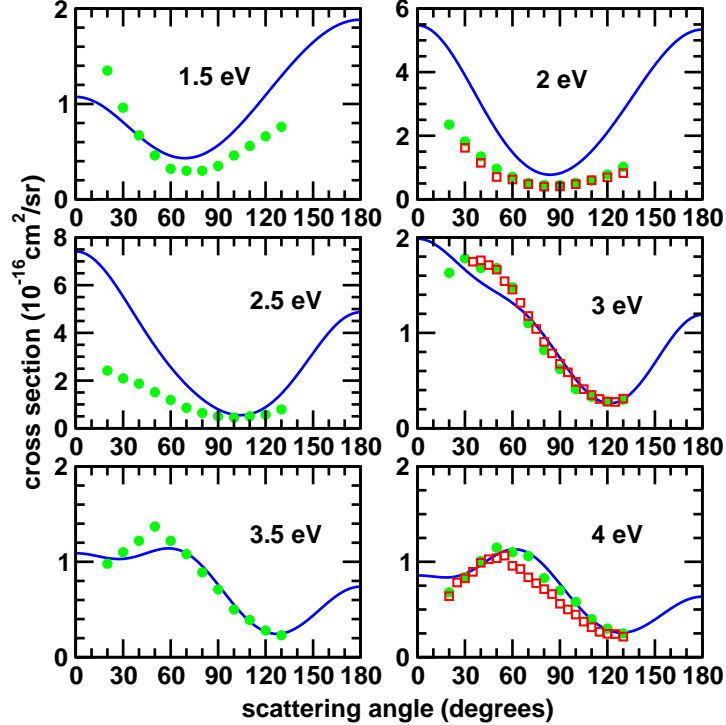


FIG. 2: (Color online) Differential cross sections for N<sub>2</sub>O at 1.5, 2, 2.5, 3, 3.5 and 4 eV. Solid line (blue), our results with 44 extra centers; circles (green) experimental data from Ref. [12] obtained at Sophia University; squares (red), experimental data from Ref. [12] obtained at the Australian National University.

obtained with 44 extra centers.

Figures 2 to 4 compare our calculated DCSs for energies from 1.5 eV to 15 eV with experimental data [4–6, 12] and with the results of *R*-matrix calculations [9]. Fig. 2 compares our results with the measurements of Kitajima and coworkers [12] for energies from 1.5 to 4 eV. At 1.5 eV, there is some agreement between theory and experiment, but at 2 and 2.5 eV, around the <sup>2</sup>Π shape resonance, the agreement worsens because of our neglect of nuclear motion. The small-angle minimum appears in the measured DCS at 3 eV but not in our calculated DCS, though we do see fairly good agreement for angles above 60°. On the other hand, at still higher energies, the calculations do begin to exhibit a minimum, and at 3.5 and 4 eV, the agreement with the experiment in the small-angle region improves. In Fig. 3, we compare our results from 5 to 10 eV with various measurements [4–6, 12] and with the calculations of Morgan and coworkers [9]. At 5, 6, and 7 eV, the agreement between our

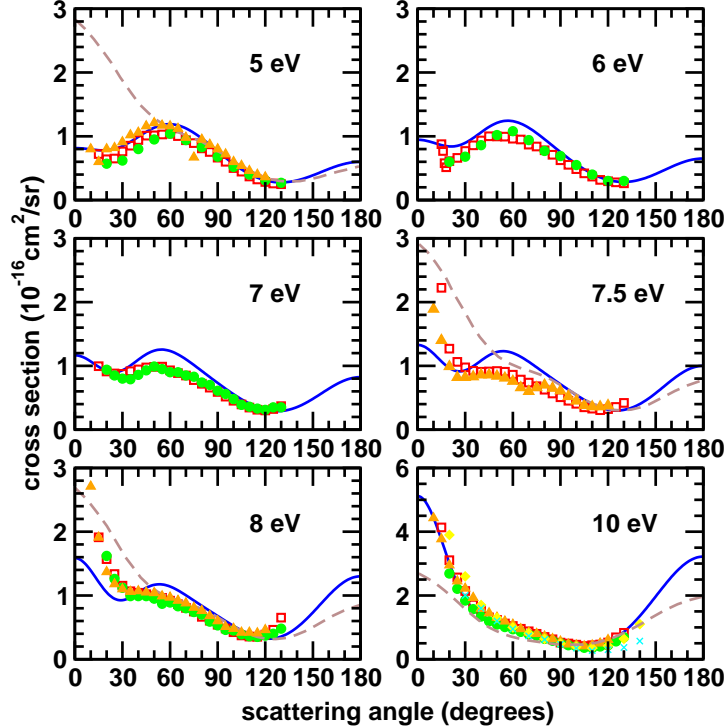


FIG. 3: (Color online) As in Fig. 2 at 5, 6, 7, 7.5, 8 and 10 eV and with the following additional results: diamonds (yellow), experimental data from Ref. [4]; triangles (orange), experimental data from Ref. [5]; crosses (light blue), experimental data from Ref. [6]; dashed line (brown), calculations from Ref. [9].

results and experiment is very good at all angles, though at 6 and 7 eV the calculated DCS appears to be too large around the maximum at  $\sim 60^\circ$ . At 7.5 and 8 eV we are again in the vicinity of a shape resonance (the  $\Sigma$  resonance), and the agreement between our results and the measurements deteriorates, but at 10 eV it is again very good. One can see from Fig. 3 that the  $R$ -matrix results of Morgan and coworkers [9] do not describe the minimum in the DCSs, nor did our own earlier calculations [10] (not shown). In fact, comparing Figs. 1 and 3, we see qualitative similarity between the DCSs of Morgan and coworkers and our results obtained without extra centers (although the latter are much smaller in the forward direction and thus in better quantitative agreement with the measured DCSs).

Figure 4 shows the DCSs at 12 and 15 eV. At these energies, the agreement between our results and the experimental data [4, 5] is good, except at small scattering angles, where our results lie below the experiment, possibly due to basis-set limitations and/or to our neglect

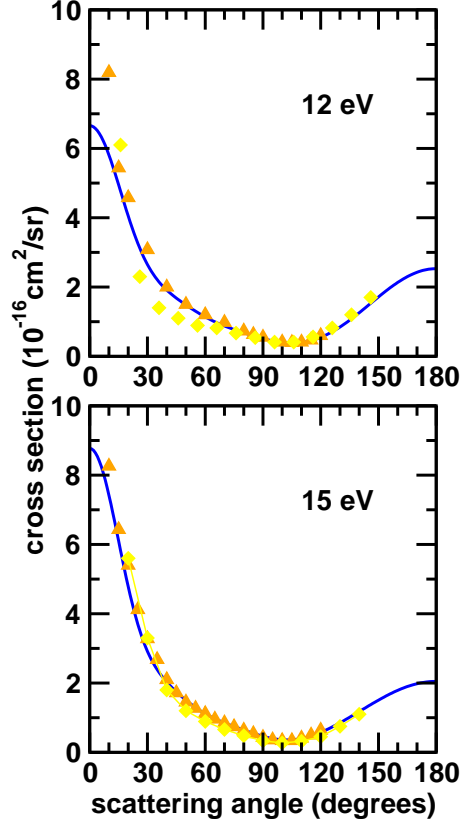


FIG. 4: (Color online) As in Fig. 3 at 12 and 15 eV.

of corrections for long-range scattering from the (small) dipole moment of  $\text{N}_2\text{O}$ .

Integral and momentum transfer cross sections are shown in Fig. 5. Despite including a much more extensive set of configurations in  $B_1$  and  $B_2$  symmetries to represent polarization effects, our present calculations place the  $^2\Pi$  shape resonance at nearly the same energy as did our previous study [10], close to the peak in the total cross section measured by Szymtkowski and coworkers [3]. The two R-matrix calculations [7, 9] place the shape resonance energy slightly lower but still close to the observed peak. As seen in Fig. 5, the calculated integral elastic and momentum transfer cross sections reproduce the shape and magnitude of the experimental data fairly well above the  $^2\Pi$  resonance energy.

In Fig. 6 we show the  $A_1$  contribution to the integral cross section from 0 to 2 eV, along with the corresponding eigenphase sum. At these energies, by far the dominant contribution to  $A_1$  comes from  $\Sigma$  symmetry. A minimum is clearly visible in the cross section near 0.2 eV, where the eigenphase sum changes sign, behavior characteristic of a Ramsauer–Townsend (RT) minimum. A low-energy minimum has indeed been observed in the total electron

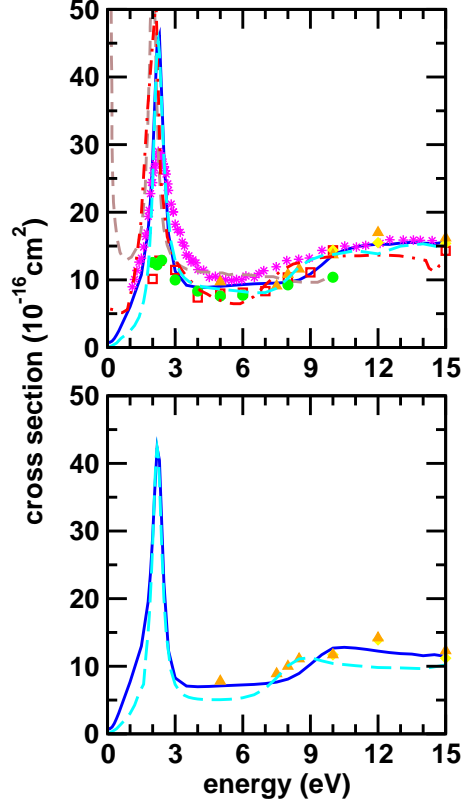


FIG. 5: (Color online) Integral (upper panel) and momentum transfer (lower panel) cross sections for  $\text{N}_2\text{O}$ . Solid line (blue), our results with 44 extra centers; stars (pink), experimental total cross section from Ref. [3]; diamonds (yellow), experimental data from Ref. [4]; triangles (orange), experimental data from Ref. [5]; circles (green) experimental data from Ref. [12] obtained at Sophia University; squares (red), experimental data from Ref. [12] obtained at the Australian National University; dot-dashed line (red), theoretical results from Ref. [7]; short dashed line (brown), theoretical results from Ref. [9]; long dashed line (light blue), theoretical results from Ref. [10].

cross section [16, 19] and, more recently, in the elastic differential cross section at  $135^\circ$  [14]. However, one expects a rise in the  $e^- - \text{N}_2\text{O}$  cross section at very low energy due to scattering by the dipole potential, so the experimental results can be, and have been, explained without invoking the RT mechanism. We also note that inclusion of corrections for dipolar scattering would alter our low-energy cross section. Thus the present results at most suggest, rather than demonstrate, the presence of an RT minimum in  $\text{N}_2\text{O}$ .

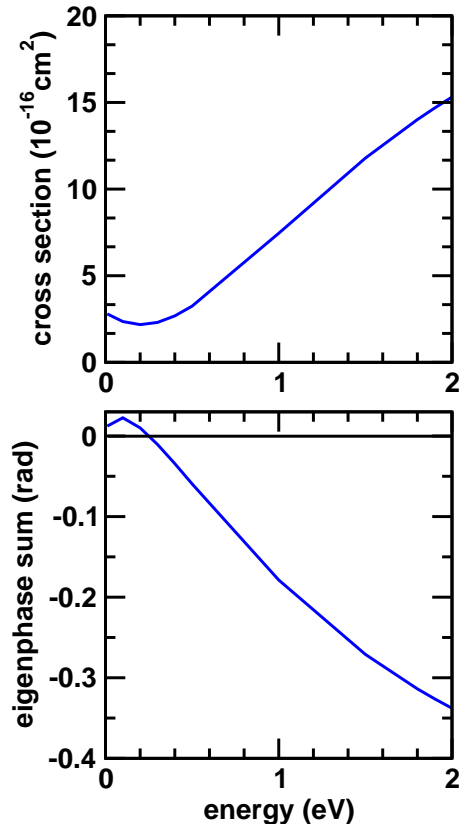


FIG. 6: (Color online) Integral cross section for the  $A_1$  symmetry (upper panel) and the corresponding eigenphase sum (lower panel).

#### IV. CONCLUDING REMARKS

The results in Figs. 1 to 3 demonstrate that we are able to reproduce the minima in the experimental DCSs of  $N_2O$  using excitations from valence orbitals into the lowest MVOs to represent polarization, as was the case for  $C_2H_4$  [23]. The present results thus give further evidence for the utility of MVOs as a simple, effective, systematically extensible particle basis. For both  $C_2H_4$  and  $N_2O$ , use of a distributed one-electron basis set improves the results; in  $N_2O$ , however, we found that the distributed basis was essential to obtaining qualitatively correct DCSs, which was not the case in  $C_2H_4$ . We believe the difference may be that in  $C_2H_4$  we already have off-axis functions (centered on the H atoms) before adding the extended basis, whereas in  $N_2O$  we start with only on-axis functions having  $m \leq 2$ . A second difference arises in the treatment of polarization in the symmetries containing the  $\pi^*$  resonance. For  $C_2H_4$ , including only relaxation of the target in the presence of an electron

trapped in the resonance orbital worked well. For  $\text{N}_2\text{O}$ , that approach gives a good location for the  $^2\Pi$  resonance but an inadequate description of higher-energy scattering. Here the difference is probably the lack of an inversion center in  $\text{N}_2\text{O}$ . In  $\text{C}_2\text{H}_4$ , the  $\pi^*$  resonance belongs to a representation whose leading partial wave is  $d$  ( $\ell = 2$ ) and which contributes only a weak background away from resonance. In  $\text{N}_2\text{O}$ , the leading wave in the representation containing the  $\pi^*$  resonance is  $p$  ( $\ell = 1$ ), and it is natural that both background scattering and the influence of polarization on that background should be stronger. Indeed, we saw in  $\text{C}_2\text{H}_4$  that polarization effects on the  $\ell = 1$  wave were very strong [23].

The present calculations, taken together with our  $\text{C}_2\text{H}_4$  results, indicate that the previous failure of calculations to reproduce the low-angle minimum seen in elastic electron scattering by various molecules [12] arises from an insufficient representation of polarization effects, sometimes in combination with an inadequate one-electron basis set. Possible explanations that have been considered in the past, including target correlation effects, vibrational effects, and explicit coupling to open electronic-excitation channels, would have entailed calculations of considerably increased complexity and difficulty. Fortunately, shortcomings in the polarization space and one-electron basis set are more readily corrected using current methodology, as we have shown.

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