Matrix variational calculations of electron scattering by C, N, and O atoms*

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Total elastic cross sections for electron scattering by ground-state C, N, and O atoms have been computed by the matrix-variational method for energies up to the first $n = 3$ excitation. Two levels of approximation are considered: single configuration (SC) and near-degenerate configuration interaction (CI). Both approximations neglect the principal effects of target-atom electric-dipole polarizability. The SC calculations are the variational equivalent of earlier close-coupling calculations including all states of the ground configuration $2s^2 2p^m$. The CI calculations augment this with configurations $2s 2p^{m+1}$ and $2p^{m+2}$. The short-range correlations introduced by the CI calculations are found to have dramatic effects on resonance structures found at low energies in SC calculations. In addition to the well-established negative-ion bound states $C^-(^4S^o)$ bound and $O^-(^2P^o)$, the CI calculations give qualitative predictions of the true location of other $2s^2 2p^{m+1}$ states: $C^-(^2D^o)$ bound; $C^-(^2P^o)$ resonance near 1 eV; $N^-(^3P)$ very near threshold, either weakly bound or a very narrow resonance; no O^- resonance. A method for precise location of these negative-ion states is proposed.

I. INTRODUCTION

A quantitative theory of low-energy electron scattering by complex atoms must take into account long-range polarization effects, a short-range correlation between the incident electron and the target atom, and electron attachment effects that lead to scattering resonances. The detailed structure of elastic and inelastic cross sections at target excitation thresholds must be described accurately. This is to be accomplished despite the impossibility of representing target-atom wave functions in simple analytic form.

Polarized orbital[1,2,3] and close-coupling[4,5] methods have been applied to electron scattering by C, N, and O atoms in the energy range of the electronic ground-state configuration. The polarized-orbital method[6] treats target-atom dipole polarizability and the resulting long-range polarization potential accurately, but involves approximations to the short-range interaction that are difficult to evaluate. As usually formulated, the polarized-orbital method cannot describe resonances. However, recent work combining the polarized-orbital and close-coupling formalisms may prove capable of surmounting this difficulty.[7]

The close-coupling method[8] is capable, in principle, of representing the full structure of the electronic continuum wave function through a series expansion in the stationary states of the target atom. In practice, this expansion is severely truncated. Until very recently the only close-coupling calculations for C, N, and O target atoms included only the ground-state configuration in this expansion.[4] This neglects the important effect of target-atom polarizability. Preliminary results of more elaborate close-coupling calculations, including

some target correlation effects[9] and a limited pseudostate representation of target polarizability, have been reported.[10]

The close-coupling method makes use of the Kohn variational principle for continuum states to produce a system of coupled integrodifferential equations, to be solved numerically for the external open- and closed-channel orbitals coupled into the series of target-atom states or pseudostates included in the wave-function expansion. A new method of similar formal structure has been developed in which the external orbitals, as well as the target states, are represented by expansion in known functions. This replaces the solution of integrodifferential equations by algebraic matrix manipulations, which can be carried out in practice for wave functions with many more terms in the target state expansion than are feasible in close-coupling calculations. Such *matrix variational* methods are an extension to electronic continuum states of computational techniques that have been very useful in applications to bound states of complex atoms and molecules. Details of this formalism have recently been reviewed.[11,12]

The present paper reports results of calculations by the matrix variational method of total electron scattering cross sections by the ground states of C, N, and O, in the energy range below the threshold of the first excited configuration. Computations have been carried out both in the single configuration (SC) approximation, comparable to earlier close-coupling calculations,[4] and in an approximation (to be denoted by CI here) that takes into account the effects of near-degenerate configuration interaction. Proper consideration of polarization effects will be left for later publications, although some preliminary results on e-O

scattering, using continuum Bethe-Goldstone equations, will be discussed here.[13]

Section II gives details of the present variational calculations. Results for total cross sections are presented in Sec. III. A study of the parametric displacement of low-energy resonances associated with negative-ion states is reported in Sec. IV. The present CI calculations appear to correct the erroneous location of these resonances given by SC calculations.

II. DETAILS OF THE CALCULATIONS

The method used here has been adequately described in recent publications.[12,14] A major innovation in the present work is that LS eigenfunctions are used throughout the calculations. This does not alter the results of the method, but makes the computations more efficient and flexible. The detailed procedure will be published elsewhere.

In outline, the matrix variational method, as implemented for the present work, constructs an $(N+1)$-electron continuum wave function by combining target-state wave functions with external oscillatory one-electron functions (orbitals) of fixed form, then superimposing $(N+1)$-electron quadratically integrable functions with coefficients determined variationally. The relative coefficients of the external open-channel orbital functions define the K matrix and other related scattering matrices, from which elastic and inelastic cross sections are obtained by standard formulas. The Hilbert space of quadratically integrable functions is constructed in a pattern of virtual excitations of a target-atom reference configuration, where such excitations increase the number of electrons by one. The entire Hilbert space is treated as the Q space in the Feshbach partitioning formalism.[15] The P space is represented by fixed external open-channel orbitals, orthogonalized to all basis orbitals used in constructing the Hilbert space, and antisymmetrized into target-atom states obtained by a configuration-interaction calculation. The partitioning formalism defines an effective Hamiltonian matrix acting in the open-channel linear space. This effective Hamiltonian contains a generalized optical potential that describes physical effects of target-atom polarization, electronic correlation, and interference between bound and free orbitals due to orthogonality.

The structure of the present calculations is very similar to those reported previously of inelastic electron scattering by He, in the energy region of the $n=2$ excited states.[16] The ground configurations of C, N, and O have the open-shell structure

$1s^2 2s^2 2p^m$, with $m = 2, 3, 4$, respectively. As in the case of the $n=2$ states of He, this leads to several states of similar structure in the same energy range, and a number of open channels are coupled by the scattering equations. For example, the ^3P ground state of O couples external s and d waves in scattering states ^2P and ^4P. Thus multichannel theory must be used even to describe elastic scattering.

A particular calculation by the present method is specified by a choice of quadratically integrable orbital basis (bound orbitals), by the configurations used to describe the target states, and by the level of virtual excitation (Bethe-Goldstone hierarchy) that defines the Hilbert-space component of the variational wave function. A range of total-symmetry quantum numbers and a range of incident electron energies must also be specified.

The bound orbital basis sets used in the present work are defined in Table I, in the form of exponential functions $r^{n-1} e^{-\zeta r}$, multiplied by spherical harmonics and spin functions. The basis orbitals were chosen in analogy to those used for similar calculations of e-He scattering.[16,17] For oxygen, the double-zeta functions of Clementi[18] for $1s$, $2s$, and $2p$ orbitals were augmented by functions with a geometric sequence of exponents with ratio 0.5. Four functions of the geometric sequence, in addition to the double-zeta basis, were found to be sufficiently complete for s, p, and d orbitals. One f orbital was added, with exponent

TABLE I. Parameters for radial basis orbitals $r^{n-1} \times e^{-\zeta r}$ for C, N, and O.

l	n	C ζ	N ζ	O ζ
s	1	7.968 97	8.938 43	10.1085
	1	5.230 90	6.118 63	7.062 27
	2	1.820 31	2.221 57	2.621 58
	2	1.167 82	1.393 27	1.627 05
	2	0.88	0.63	0.8
	2	0.484	0.2835	0.4
	2	0.2662	0.1276	0.2
	2	0.1464	0.057 41	0.1
p	2	2.726 25	3.267 41	3.681 27
	2	1.255 72	1.505 85	1.653 72
	2	0.5985	0.7125	0.8
	2	0.2843	0.3384	0.4
	2	0.1350	0.1607	0.2
	2	0.064 14	0.076 36	0.1
d	3	1.000	3.0	1.45
	3	0.500	1.5	0.725
	3	0.250	0.75	0.3625
	3	0.125	0.375	0.181 25
f	4	1.5	2.25	1.4

chosen to give approximately stationary values of trial cross sections. For C and N the same number of basis functions were used. For carbon, geometric ratios 0.55, 0.475, and 0.5 were used, respectively, for the s-, p-, and d-orbital basis sets. For nitrogen these ratios were 0.45, 0.475, and 0.5, respectively.

For single configuration (SC) calculations, only the ground-state configuration $1s^2 2s^2 2p^m$ is included in the representation of target atom states. Ortho-normal s and p orbitals were obtained from matrix Hartree-Fock solutions for the atomic ground states. The Hartree-Fock one-electron Hamiltonian was diagonalized in the basis described above to determine the remaining orthonormal set of unoccupied orbitals. For SC calculations, the Hilbert-space part of the scattering wave function is defined by [0], indicating that no virtual excitations of the target configuration are included. These calculations are the variational equivalent of $(N+1)$-electron Hartree-Fock calculations, with one electron in a continuum state. All scattering states formed by antisymmetrizing an external s, p, d, or f orbital into the states of the target configuration are included in the calculations. These target states are ^3P, ^1D, and ^1S for C and O; $^4S^o$, $^2D^o$, $^2P^o$ for N. The energy range below the first excited configuration $(2p \rightarrow 3s)$ was considered. The SC approximation cannot describe target-atom electric dipole polarization, so effects of the polarization potential are neglected. For C and O the ^3P ground state has a finite quadrupole moment and a long-range (r^{-3}) static quadrupole potential is present in the SC approximation.

The CI calculations reported here augment the ground-state configuration $1s^2 2s^2 2p^m$ by the configurations $1s^2 2s 2p^{m+1}$ and $1s^2 2p^{m+2}$ of the same atomic shell $(n=2)$. Configuration interaction between the nearly degenerate $2s^2 2p^m$ and $2p^{m+2}$ configurations is known to be an important effect in stationary-state calculations. The opposite parity configuration $1s^2 2s 2p^{m+1}$ does not combine with the others, but contributes a near-degenerate term to the electric dipole polarizability. The Hilbert space for the CI calculations, still defined by [0], omits virtual excitations, but includes all $(N+1)$-electron configurations obtained by adjoining any unoccupied orbital to any of the target-state configurations. From experience with bound-state calculations, the CI approximation should be a more stable base for further exploration of polarization and correlation effects than the SC approximation, which neglects near-degeneracy effects (zeroth order in $1/Z$ perturbation theory).

It should be noted that in the present work whenever an electronic configuration is represented in the wave function, all possible states and all in-

dependent coupling schemes of this configuration are automatically included in the calculations.

III. RESULTS FOR CROSS SECTIONS

A. Carbon

Figure 1 compares SC and CI calculations of the total ground-state cross section of carbon with the polarized-orbital calculation of Henry.[3] The present SC calculations, using the matrix variational method, give results in substantial agreement with earlier SC calculations by the close-coupling method.[4] No experimental data is available for comparison. Since polarization is neglected in the SC approximation and only partially included in the CI approximation, it is expected that full inclusion of polarization effects would move these curves downward toward the polarized-orbital result, except for the effects of resonances, which cannot be described by the polarized-orbital method.

Figure 1 shows that the low-energy resonances are sensitive to near-degeneracy correlation effects. The ^1S target state threshold is also sensitive to such effects. The computed thresholds (CI) are indicated in Fig. 1, with the SC result for ^1S shown in parentheses. The computed $^5S^o$ threshold is significantly below its experimental value.

Figure 2 shows the sum of eigenphase shifts for $^2D^o$ and $^2P^o$ scattering states. The eigenphase sum is half the complex phase of the determinant of the S matrix, which rises abruptly through 2π radians near a narrow resonance. Hence, the eigenphase sum increases by π radians for a multichannel resonance. It can be seen in Fig. 2 that the CI calculation has pushed the $^2D^o$ resonance below
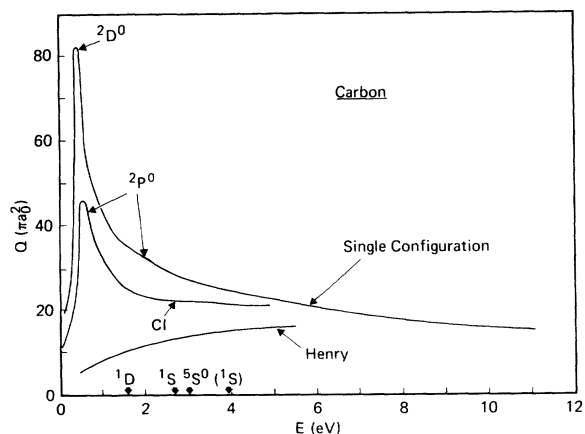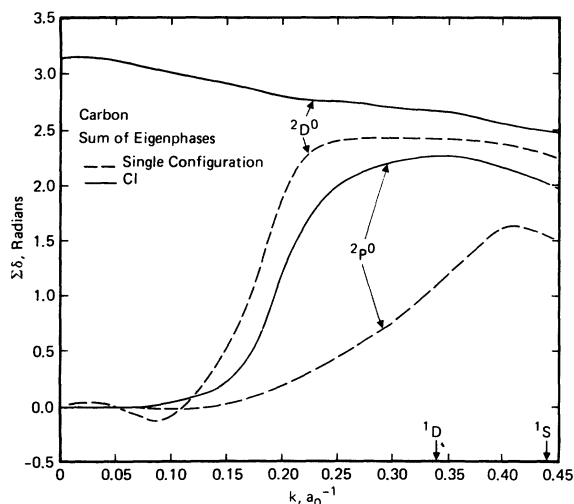

FIG. 1. e-C(^3P) total cross section.

FIG. 2. e-C, sum of eigenphases for $^2D^o$ and $^2P^o$ scattering states.

FIG. 4. e-N, sum of eigenphases for ^3P scattering state.

the ^3P target ground-state threshold. This is in agreement with recent experimental data indicating a $^2D^o$ bound excited state of C⁻ at 0.035 eV below the C ground state.[19] The broad $^2P^o$ resonance that appears only as a shoulder in the SC calculation is narrowed and moves down closer to the threshold. More accurate calculations will change its location and width quantitatively, but it is unlikely to get substantially closer to the $^2D^o$ metastable state. Since there is no experimental evidence of a $^2P^o$ bound state of C⁻, the present results predict a low-energy resonance of this description. The predominant electronic configuration should be $1s^22s^22p^3$.

B. Nitrogen

Figure 3 compares SC and CI calculations of the total ground-state cross section of nitrogen

with recent multiconfiguration close-coupling (MCC) results of Ormonde et al.,[5] with the polar-ized-orbital calculation of Henry,[3] and with ex-perimental data of Neynaber et al.[20] Figure 4 shows a trend in the N⁻ (^3P) resonance similar to the $^2D^o$ resonance of C⁻. However, the present calculations cannot resolve the question of whether this state is bound or not. Detailed bound-state calculations[21] show that the relative location of N⁻ (^3P) and N(^4S) is sensitive to three-electron correlation effects, not included in the present work. There is no experimental evidence of a bound state of N⁻. Calculations given below (Sec. IV) indicate that if the N⁻ (^3P) state is a resonance just above threshold, it will be extremely narrow, and may be impossible to observe with present experimental techniques.

The MCC calculation of Ormonde et al.[5] is simi-lar in scope to the present CI calculation, but in-cludes only the ^4P term of the configuration $1s^22s2p^4$. Terms from configurations $2s^22p^23s$
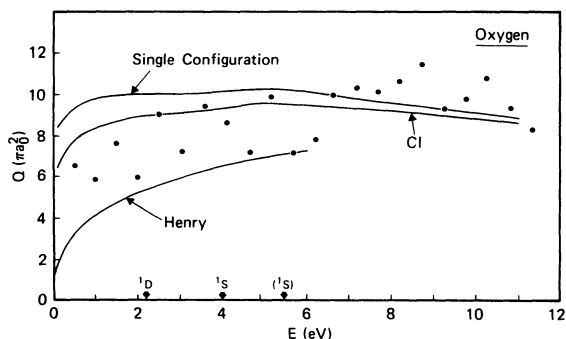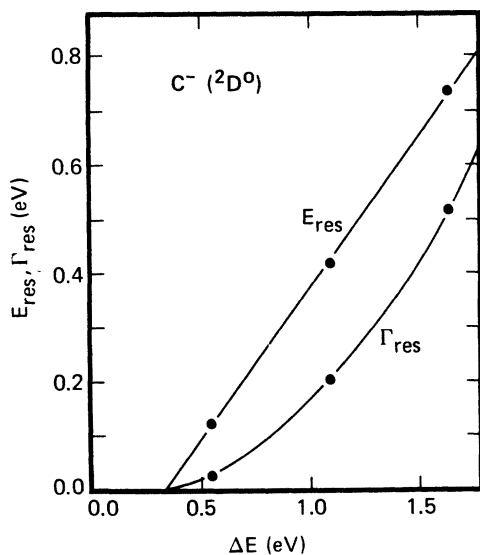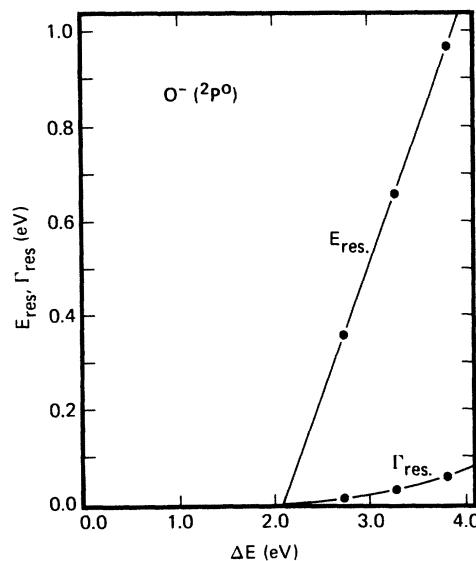

FIG. 3. e-N($^4S^o$) total cross section.

FIG. 5. e-O(^3P) total cross section.

FIG. 6. $C^-(^2D^o)$ resonance energy and width.

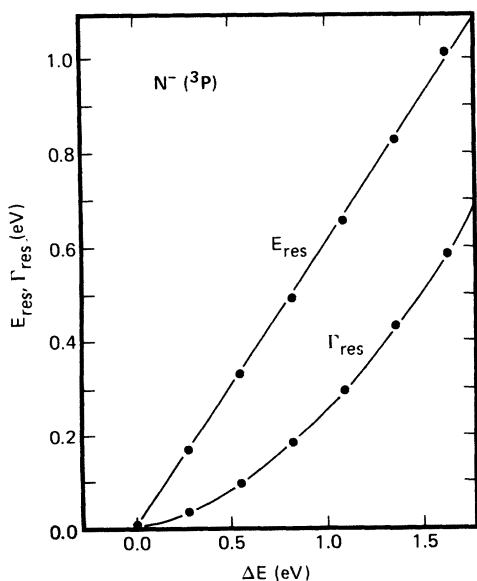FIG. 8. $O^-(^2P^o)$ resonance energy and width.

and $2s^2 2p^2 3d$, which contribute to the electric-dipole polarizability, are also included. As shown in Fig. 3, the CI and MCC results agree well above the ^2P excitation threshold, but the MCC results at low energies do not include enough points to locate the expected ^3P resonance, which appears to influence the lowest MCC point.

Although it gives no information regarding a possible ^3P resonance, the polarized-orbital calculation of Henry,[3] shown in Fig. 3, indicates that long-range polarization effects will lower the CI or MCC curves. Some additional reason must be

FIG. 7. $N^-(^3P)$ resonance energy and width.

invoked to account for the fact that the polarized-orbital curve lies consistently above the experimental data and outside the indicated error bars.

C. Oxygen

Figure 5 compares SC and CI calculations of the total ground-state cross section of oxygen with the polarized-orbital calculation of Henry[2] and with the experimental data of Sunshine et al.[22] No low-energy resonances appear in either the SC or CI results, and probably not in the experimental data. Comparison with the polarized-orbital results indicates that an accurate treatment of target-state polarizability and the resulting polarization potential will be essential before quantitative results can be obtained. There is no obvious explanation of the fact that the polarized-orbital cross section lies *below* experiment for O but *above* for N. The absence of resonant structure in the SC and CI calculations is in accord with the fact that the only possible O^- state of configuration $1s^2 2s^2 2p^5$ is identified with the $^2P^o$ ground state, bound by 1.5 eV with respect to $O(^3P)$. Preliminary results of continuum Bethe-Goldstone calculations, allowing for virtual excitation of the $2p$ subshell,[13] indicate that the true e-O total cross section at low incident energy is close to the polarized-orbital curve.

IV. PARAMETRIC DISPLACEMENT OF RESONANCES

The exact location of negative-ion bound states or resonances with respect to neutral atom energy levels can depend very sensitively on two- and

three-electron correlation effects.[21] Since three-electron effects are systematically neglected in the present scattering calculations, it should be valid to treat the resulting energy displacements as parameters eventually to be determined from experimental data. In order to explore the qualitative nature and possible magnitude of such effects, the resonances associated in the present work with the $2s^2 2p^{m+1}$ ground configurations of C^-, N^-, and O^- have been examined as functions of a parameter ΔE, added into the diagonal energy-matrix elements of Hilbert-space wave functions of this particular configuration. Resonance energies E_{res} and widths Γ_{res} were computed by the multichannel resonance search method used in the present work.[23] This method defines the resonance parameters in terms of the value and slope of the sum of eigenphases as a function of k (electron momentum or wave number) at the point of maximum slope. The orbital basis sets used for these calculations were somewhat reduced from those listed in Table I, retaining only six s orbitals and four p orbitals, together with four d orbitals and two f orbitals.

Results of parametrized resonance CI calculations are shown in Figs. 6, 7, and 8 for C^- $(^2D^o)$, N^- (^3P), and O^- $(^2P^o)$, respectively. In each case E_{res} (ΔE) is well fitted by a straight line, and Γ_{res} (ΔE) goes smoothly to zero at the point where E_{res} vanishes. These properties verify the internal consistency of the parametrization, and make it possible to extrapolate from the resonance re-
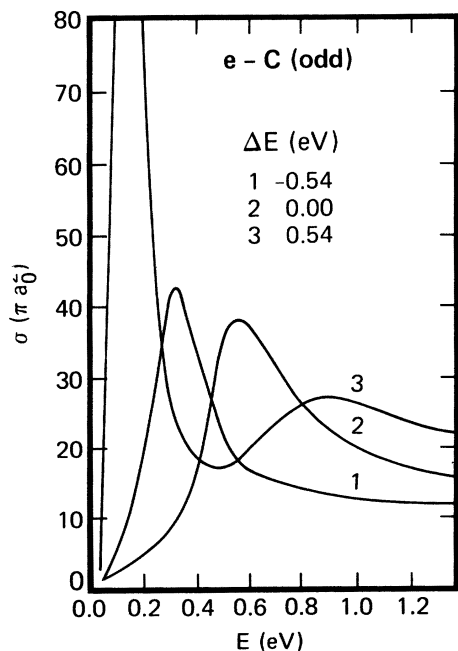
gion to the region of bound or metastable negative-ion states, below the neutral ground-state threshold.

For a completely accurate calculation, the true location of a negative-ion state or resonance should be given by the value of E_{res} when $\Delta E = 0$. From Figs. 6, 7, and 8 these values would be -0.2 eV for C^- $(^2D^o)$, 0.0 eV for N^- (^3P), and -1.2 eV for O^- $(^2P^o)$. These values are in reasonable qualitative agreement with the experimental estimate[21] of -0.035 eV for C^- $(^2D^o)$, the fact that N^- (^3P) has never been observed, and the well established experimental value -1.47 eV for O^- $(^2P^o)$.

These results provide the basis for a new method of locating negative-ion states near threshold.[24] Electron-scattering cross sections can be computed for a range of values of the parameter ΔE and compared with experimental data in the energy region several volts above threshold. Resonance
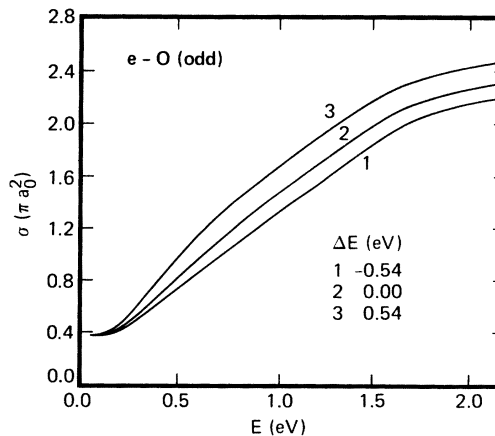

FIG. 10. e-N($^4S^o$) even-parity partial cross section.

FIG. 9. e-C(^3P) odd-parity partial cross section.

FIG. 11. e-O(^3P) odd-parity partial cross section.

parameters can also be computed as functions of ΔE. If both experimental scattering data and the theoretical calculations are of sufficiently high accuracy, comparison of scattering data will determine a best value of ΔE. Then the computed curves $E_{res}(\Delta E)$ can be used for accurate extrapolation to the true energy of the negative-ion state.

For this method to succeed, scattering cross sections must be reasonably sensitive to the parameter ΔE. Figures 9, 10, and 11 show the results of CI calculations of partial cross sections (one parity only) for C, N, and O, respectively,

computed for a range of ΔE about zero. These figures indicate a significant variation of the partial cross sections in an energy range where accurate experimental data may be obtainable.

It should be emphasized that the present calculations (SC and CI), which neglect or include only partially the electric-dipole polarization potential, are not expected to be sufficiently accurate for the experimental comparison proposed here. Calculations at the level of the valence-shell Bethe-Goldstone approximation[12,13] may be adequate for this purpose.

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