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Theoretical study of electron-impact excitation of $N_2{}^+$

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We report the results of an *ab initio* treatment of electron-impact excitation cross sections for the process $e^- + N_2^+(X\,{}^2\Sigma_g^+) \rightarrow e^- + N_2^+(B\,{}^2\Sigma_u^+)$ from 5.0 to 40 eV. The dynamically important low-order partial wave components of the scattering amplitude were obtained from multistate close-coupling calculations with correlated target wave functions. The calculations were carried out using a modification of the complex Kohn variational method. The higher-order partial-wave components, which are essential for computing converged cross sections for optically allowed transitions such as this, were efficiently evaluated by an asymptotic Coulomb-Born approximation. Of the widely differing sets of experimental cross sections reported for this process, our calculations are in excellent agreement with the most recent measurements.

I. INTRODUCTION

Despite the important role that electron collisions with molecular ions play in many low-temperature plasmas, little progress has been made in the development of theoretical methods for the calculation of accurate cross sections, especially for electronic excitation. Reliable theoretical methods are exceptionally important because of the extreme difficulty of experiments in this area. A good example is afforded by $N_2{}^+$. The $v=0 \rightarrow v=0$ transition of the first negative system $(B\,{}^2\Sigma_u^+ \rightarrow X\,{}^2\Sigma_g^+)$ at 391.4 nm is an intense band in nitrogen-containing plasmas and figures prominently in most diagnostic measurements. There have been several experimental determinations of the electron impact cross section for the $X \rightarrow B$ transition. However, they differ from one another by almost two orders of magnitude.[1-4] The problem, of course, is that measurements made under plasma conditions are done with less than well-characterized ion sources and give only indirect information about cross sections. In deducing excitation cross sections from optical emission measurements, certain assumptions must be made about state mixtures, cascade processes, and branching ratios that can potentially introduce large systematic uncertainties into the final results. Thus, the need for accurate theoretical treatments is especially important.

There has been a concerted effort in recent years by several groups to develop a theoretical method capable of determining accurate cross sections for various electron-molecule collision processes.[5-8] Substantial progress has recently been made in the study of electronic excitation,[9-11] as well as collisions with polyatomic targets.[12] The corresponding electron–molecular-ion collision problem, by contrast, has received almost no theoretical attention. There has, however, been a substantial amount of work on molecular photoionization processes. Photoionization cross sections involve dipole matrix elements between a final-state wave function made up of continuum orbitals and a *bound* initial state. The presence of a bound wave function in the formulation is a considerable simplification. On the one hand, it has allowed the use of various L^2 methods, such as the method of complex basis functions[13] and the method of moments,[14] which avoid the direct solution of the scattering problem and its attendant specification of asymptotic boundary conditions. Furthermore, not only do dipole selection rules limit the number of symmetry components of the final state wave function that have to be treated in photoionization, but the bound initial-state wave function effectively puts a box around the target and thus confines the number of partial-wave components needed to obtain a meaningful result. In contrast, the direct electron-ion scattering problem may require many partial-wave components to produce a meaningful result. This is especially true in the case of dipole-allowed transitions, which are most important in plasma diagnostics because of their optical signature and correspondingly large cross sections.

We have extended the complex Kohn variational method to the study of ionic molecular targets. The complex Kohn method has been used with considerable success in the study of electron scattering from neutral molecules.[8] It has been used to study scattering from polyatomic systems, such as methane[12] and formaldehyde,[15] producing accurate cross sections. More importantly, it has been used to treat electronic excitation beyond the static-exchange approximation.[11] In Sec. II we will show how the complex Kohn method can be easily extended to the case of molecular-ion targets by modifying the asymptotic form of the trial wave function to account for the long-range Coulomb interaction between incident electron and ionic target. We will also outline a method for incorporating the contributions of the high-order partial-wave components necessary to obtain converged excitation cross sections for optically allowed transitions. In Sec. III we describe our calculations on the $e^- + N_2^+$ system and we compare our results with available experiments. In this section we also discuss the modifications of the Kohn method which are required when open channels are not included in the close-coupling expansion. Section IV contains some concluding remarks.

II. THEORETICAL DEVELOPMENT

The complex Kohn method is an algebraic variational technique which, over the last few years, has been developed into a powerful new approach for studying both heavy-particle (reactive) collisions[16] and electron-scattering problems.[8,11,12,15] Although based on the original Kohn variational principle, it is formulated with complex, outgoing wave boundary conditions. This simple modification eliminates a long-standing problem with the Kohn method—that of spurious resonances.[17] Numerical anomalies in the complex Kohn approach only occur for unphysical choices of the variational basis-set parameters[18] and, in contrast to the original Kohn method, disappear as the trial function is improved. We first give a brief summary of the major aspects of the complex Kohn method as applied to neutral targets.

A trial wave function of the following form is chosen:

$$\Psi_\Gamma(\mathbf{r}_1,\ldots,\mathbf{r}_{N+1})=\sum_{\Gamma'}\mathcal{A}[\chi_{\Gamma'}(\mathbf{r}_1,\ldots,\mathbf{r}_N)F_{\Gamma\Gamma'}(\mathbf{r}_{N+1})] + \sum_\mu d_\mu^\Gamma \theta_\mu(\mathbf{r}_1,\ldots,\mathbf{r}_{N+1}) . \quad (1)$$

The first sum runs over energetically open states of the N-electron target which are described by wave functions χ_Γ. These may be single-configuration, Hartree-Fock wave functions, or correlated, multiconfiguration wave functions. The functions θ_μ in the second sum are a set of square-integrable, $(N+1)$-electron functions that are used to incorporate closed-channel and correlation effects. In practice, these terms are included indirectly by construction of an optical potential.[8] The $F_{\Gamma\Gamma'}$ are channel continuum functions whose asymptotic behavior defines the essential scattering parameters from which cross sections are obtained.

In the complex Kohn method, the channel continuum functions are further expanded as linear combinations of both square-integrable (Gaussian) basis-set functions as well as incoming and outgoing continuum functions which behave asymptotically as Ricatti-Bessel functions, that is, $\sin(kr - l\pi/2)$ and $\exp[i(kr - l\pi/2)]$, respectively.

The unknown parameters in the Kohn method are the linear coefficients of the various bound and continuum basis-set functions in the trial wave function.[8] These are determined by inserting the trial wave function into a stationary principle, and solving the resulting set of algebraic equations. The most time-consuming step in the Kohn method, as in any algebraic variational method, is the evaluation of the various matrix elements (bound-bound, bound-free, free-free) of the Hamiltonian. To accomplish this task efficiently, we make judicious use of separable expansions for both the exchange and optical potential terms of the Hamiltonian to rigorously limit their appearance solely to matrix elements over the square-integrable part of the basis.[19] The remaining direct terms involving continuum functions are evaluated by an adaptive numerical three-dimensional (3D) quadrature scheme. The details of this procedure are fully described elsewhere.[12]

The use of Ricatti-Bessel functions in the trial wave function is not appropriate for describing the interaction between an electron and an ionic target. The functional form of the channel continuum wave function must reflect the long-range Coulomb interaction. Therefore, the regular and outgoing Ricatti-Bessel functions used for neutral targets must be replaced by functions which behave as

$$\begin{aligned} f_l &\sim F_l(\rho,\eta) , \\ h_l &\sim G_l(\rho,\eta)+iF_l(\rho,\eta) , \end{aligned} \quad (2)$$

where F_l and G_l are the regular and irregular Coulomb functions whose asymptotic form is

$$\begin{aligned} F_l &\sim \sin(\rho-\eta\ln 2\rho - l\pi/2+\sigma_l) , \\ G_l &\sim \cos(\rho-\eta\ln 2\rho - l\pi/2+\sigma_l) , \end{aligned} \quad (3)$$

with $\rho=kr$, $\eta=Z/k$, and $\sigma_l=\arg[\Gamma(1+l+i\eta)]$. Note that the form chosen for h_l causes it to behave asymptotically as a purely outgoing wave. Thus, this modification will preserve the essential feature of the complex Kohn method, that is, the elimination of spurious singularities.

The conventional choice for the outgoing wave continuum function, h_l, defined in Eq. (2) is to simply multiply the irregular Coulomb (or Ricatti-Bessel) function by an exponential cutoff. Although previous calculations on neutral molecules with the complex Kohn method showed little sensitivity to the form of the cutoff functions, our initial calculations on Coulomb systems revealed a much larger dependence on these functions. This sensitivity is evident in cases where many partial waves are required. We therefore sought a more physical choice for the "regular" outgoing continuum function. To help motivate our final choice, we note that the exact wave function (in a simple one-channel case) behaves as

$$\Psi_l = F_l + \mathcal{G}_l^+ V\Psi_l \rightarrow F_l + h_l \int VF_l + \cdots , \quad (4)$$

where $\mathcal{G}_l^+$ is the partial-wave Coulomb Green's function. This suggests that a more physical form for the outgoing continuum function would be to simply use a function of the form

$$h_l = \mathcal{G}_l^+ W / \int WF_l , \quad (5)$$

where the test "potential" function must diverge less strongly than $1/r^2$ at the origin and go to zero faster than $1/r$ asymptotically, but is otherwise arbitrary. This choice for the outgoing continuum function is similar in spirit to that recently proposed by Sun *et al.*[20] Numerical details of how we efficiently construct these functions are presented elsewhere.[21] We have found much less sensitivity to the choice of the potential function W than to the cutoff functions employed in the original Kohn method. In this work, we used $W(r)=\exp(-r)$.

The modified complex Kohn method has a completely analogous form to that used for neutral-target scattering. In particular, the correct outgoing wave behavior of the wave function is incorporated within the trial function. It is important to bear in mind that the implied expansion over partial waves only refers to the asymptotic wave function. Partial-wave expansions are not used to expand the interaction potentials. This allows highly nonspherical targets to be considered, and the convergence will be comparable to that seen in neutral systems.

A fundamentally important problem is the prediction of cross sections for the excitation of electronic states which are connected to the ground state by a dipole transition. Indeed, it is the radiation from these states which is often used as a probe of plasma conditions. Therefore, any formalism for studying electron-ion collisions must be capable of addressing this problem to be of any practical use.

Electron-impact excitation of states which are dipole connected to the ground state can require many partial-wave components to produce converged cross sections, even at low impact energies, because of the effective long-range $1/r^2$ behavior of the transition potential. This long-range coupling of high-order partial waves is not a dynamical coupling that involves other excited states, so the high-angular-momentum components can usually be treated in the lowest order of perturbation theory, the first-order Born approximation. Thus, it is sufficient to use a hybrid treatment where the lowest-order partial waves are treated dynamically and the high-order partial waves, needed for convergence, are computed in the Born approximation.[22] For neutral molecules, this "dipole Born approximation" can be carried out analytically and used to obtain converged cross sections for dipole-allowed transitions.[23] Only the lowest partial-wave components need be accurately treated.

For molecular ions, this "dipole Born" correction is much more difficult to carry out because the unperturbed scattering states are Coulomb wave functions and no analytic treatment of the matrix elements is possible. Furthermore, for molecular ions, the transition potential is a complicated, nonspherically symmetric operator. The numerical evaluation of matrix elements involving a complicated nonspherical potential and hundreds of partial-wave Coulomb functions would actually be more computationally intensive than any other aspect of the calculation. However, such a brute force approach is not necessary.

Consistent with the use of the Coulomb-Born approximation for the high-l components of the scattering amplitude is the asymptotic approximation of the transition potential itself:

$$\begin{aligned} V_{\Gamma\to\Gamma'}(\mathbf{r}) &= \sum_{i=1}^{N} \left\langle \chi_\Gamma(\mathbf{r}_1,\mathbf{r}_N) \left| \frac{1}{|\mathbf{r}-\mathbf{r}_i|} \right| \chi_{\Gamma'}(\mathbf{r}_1,\mathbf{r}_N) \right\rangle \\ &\cong \frac{\boldsymbol{\mu}\cdot\mathbf{r}}{r^3} , \end{aligned} \tag{6}$$

where $\boldsymbol{\mu}$ is the transition moment between the target electronic states χ_Γ and $\chi_{\Gamma'}$. This approximation follows from retaining only the dipole term in a multipole expansion of $1/|\mathbf{r}-\mathbf{r}_i|$. (The monopole term vanishes because of the orthogonality of χ_Γ and $\chi_{\Gamma'}$.) With this approximation, we can easily evaluate the Coulomb-Born T-matrix elements as

$$\begin{aligned} T^B_{lm,l'm'} &= \frac{2}{\sqrt{k_\Gamma k_{\Gamma'}}} \int F_l(r) Y^*_{lm}(\hat{\mathbf{r}}) \frac{\boldsymbol{\mu}\cdot\mathbf{r}}{r^3} F_{l'}(r) Y_{l'm'}(\hat{\mathbf{r}}) dr\, d\hat{\mathbf{r}} \\ &= \frac{2}{\sqrt{k_\Gamma k_{\Gamma'}}} |\boldsymbol{\mu}| \left[\frac{4\pi(2l+1)(2l'+1)}{3} \right]^{1/2} (-1)^m Y^*_{1m-m'}(\hat{\mu}) \begin{bmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l & 1 & l' \\ -m & m-m' & m' \end{bmatrix} \\ &\quad \times \int F_l(r) F_{l'}(r) \frac{1}{r^2} dr , \end{aligned} \tag{7}$$

where the T-matrix elements are defined such that the total cross section is given by

$$\sigma_{\Gamma\to\Gamma'} = \frac{4\pi}{k^2_\Gamma} \sum_{l',m',l,m} |T_{lml'm'}|^2 . \tag{8}$$

In this work, we used Eq. (7) for computing T-matrix elements for values of $l,l'>6$. Note that the $3j$ symbols in Eq. (7) restrict the nonzero Coulomb-Born T-matrix elements to those with $l'=l\pm1$.

III. NUMERICAL DETAILS

A. Target wave functions

Examination of the $N_2{}^+$ electronic spectrum shows the ground state ($X\,{}^2\Sigma_g^+$) and two low-lying states ($A\,{}^2\Pi_u$ and $B\,{}^2\Sigma_u^+$) well isolated from the higher excited states. The next manifold of excited states lies ~5 eV above the B state. For the purpose of this study, we excluded these higher states from consideration and coupled the three lowest electronic states. These three states have similar potential-energy curves and equilibrium internuclear separations.

Near their equilibrium separation, each of these states is nominally described by a single-configuration wave function, corresponding to the removal of an electron from one of the valence orbitals of N_2:

$$\begin{aligned} X&: \; 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g \;\; (3\sigma_g^{-1}) \\ A&: \; 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^3 3\sigma_g^2 \;\; (1\pi_u^{-1}) \\ B&: \; 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u 1\pi_u^4 3\sigma_g^2 \;\; (2\sigma_u^{-1}) \end{aligned} \tag{9}$$

Although these simple designations are qualitatively useful, they are inadequate for accurate studies. First, there is the well-known misordering of the Koopman's ionization potentials of the X and A states.[24] Moreover, we found that we could not obtain a reasonable value for the $X \rightarrow B$ transition moment with single-configuration wave functions, no matter how the occupied molecular orbitals were chosen. For optically allowed transitions, it is essential to use target wave functions that give the correct transition moment.

The target wave functions we finally used were obtained from configuration-interaction (CI) calculations carried out in a standard Gaussian basis set consisting of the Dunning $[9s5p/5s3p]$ nitrogen basis set[25] with one d function ($\alpha_d = 0.98$). All calculations were carried out at the experimental equilibrium internuclear separation of $N_2{}^+$, 1.131 Å.[26] We began by constructing a compact set of molecular orbitals. We initially carried out a multireference CI calculation consisting of single excitations relative to the reference configurations given in Eq. (9) and then obtained the natural orbitals from the averaged one-particle density matrices for the X and B states. This orbital set was truncated on the basis of occupation number to a final set consisting of three σ_g, two σ_u, one π_u, and one π_g molecular orbitals. The target wave functions we used were obtained by freezing the $1\sigma_g$, $1\sigma_u$ and $2\sigma_g$ orbitals and carrying out, in this small molecular orbital basis set, a CI calculation that included all single and double excitations from the dominant configurations for the X and B states. This gave a value of 4.13 eV for the $X \rightarrow B$ vertical transition energy, while the experimental value is 3.16 eV.[27] Our calculated electronic transition moment was 0.836 a.u. The accurate value is 0.714 a.u. (Ref. 28). We would not expect the error in the calculated transition energy to significantly effect the cross section, except at impact energies very close to threshold.

B. Scattering basis and orthogonality constraints

The Kohn trial wave function is determined by specifying the square-integrable and continuum basis functions which are used to expand the scattering functions $F_{\Gamma\Gamma'}$ of Eq. (1). The square-integrable basis-set functions were chosen by augmenting the original target basis-set with additional Gaussian functions to provide flexibility in describing the scattering wave function. This additional set consisted of three s-type and three p-type Gaussians on each of the nitrogen centers $[\alpha_s = 3.0, 1.5, 0.5, \alpha_p = 3.0, 1.5, 0.25]$ and three s-type, two p-type, and two d-type Gaussians at the center of charge $[\alpha_s = 2.0, 0.5, \alpha_p = 0.15, 0.075, 0.03, \alpha_d = 1.0, 0.05]$. Continuum basis functions [Eq. (2)] up to $l = 6$ were included in the scattering function.

The continuum functions f_l and h_l were orthogonalized both to the square-integrable part of the scattering basis as well as to the orbitals used to expand the target wave functions. Whereas the first orthogonalization simply amounts to a unitary transformation among the basis functions which leaves the T-matrix elements unchanged,[29,30] orthogonalization of the continuum orbitals to the target orbitals can represent an unphysical constraint on the total wave function. In our formulation of the Kohn method, these unphysical constraints are relaxed by including in the second sum of Eq. (1) appropriate $(N+1)$-electron configurations made up from the target orbitals. The set of all such "orthogonality relaxing" terms can be obtained by constructing the $(N+1)$-electron configurations, which are consistent with the Pauli principle and the total space and/or spin symmetry, that result from taking the direct product of a target mole- cular orbital and all N-electron configurations used in the target wave functions. For example, the dominant configuration for the B state is $(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u 1\pi_u^4 3\sigma_g^2)\,{}^2\Sigma_u^+$. Thus, in overall ${}^1\Pi_u$ symmetry, we need the configuration $(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u 1\pi_u^4 3\sigma_g^2 1\pi_g)\,{}^1\Pi_u$. However, we included only those terms generated from the dominant configuration for each of the three target state wave functions from the list of all possible orthogonality relaxing terms. We have shown elsewhere that inclusion of orthogonality terms generated from target state configurations with small coefficients in the CI expansion, can lead to unphysical cross sections at intermediate energies. The orthogonality relaxing terms we exclude from our calculation would introduce coupling to open channels which are not explicitly included in the close-coupling expansion.[31]

C. Results

The T matrix should converge, for increasing l, and l', to the Coulomb-Born approximation, Eq. (7). Individual T-matrix elements were examined to determine when convergence to this limit was obtained. We found that for $l, l' > 6$ the T-matrix elements had converged to the Coulomb-Born values to better than 1%. In the final calculation of the cross section, all T-matrix elements with

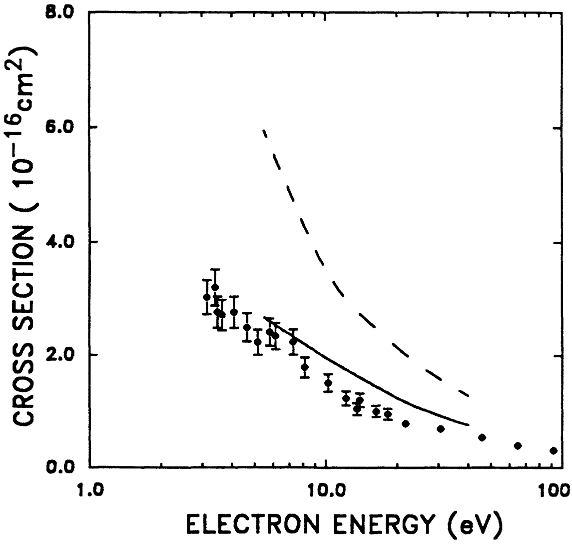

FIG. 1. Excitation cross section vs electron energy for the process $e^- + N_2{}^+(X\,{}^2\Sigma_g^+,\ \nu=0) \rightarrow e^- + N_2{}^+(B\,{}^2\Sigma_u^+,\ \nu=0)$. Solid line, present results; dashed line, Coulomb-Born approximation; solid circles, results of Crandall *et al.* (Ref. 4).

$l,l' \leq 6$ were obtained from three-state coupled-channel calculations. These calculations included contributions from the $^{1,3}\Sigma_g^+$, $^{1,3}\Sigma_u^+$, $^{1,3}\Pi_g$, and $^{1,3}\Pi_u$ total symmetry components which were weighted by appropriate space and spin degeneracy factors in computing the excitation cross sections. All T-matrix elements with $l,l' > 6$ were calculated using Eq. (7).

Our calculations were carried out within the framework of the fixed-nuclei and Franck-Condon approximations. Cross sections calculated from our fixed-nuclei T-matrix elements therefore correspond to total cross sections summed over all vibrational and rotational levels of the final state. In order to compare with experiments that monitor 391.4-nm radiation from the $v=0 \rightarrow v=0$ band of the $B \rightarrow X$ transition, we multiplied our results by 0.65, which is the measured value of the Franck-Condon factor, q_{00}^{XB}, between the ground vibrational levels of the X and B states.[32] In Fig. 1, we show our integral cross sections as a function of electron energy. The pure Coulomb-Born values are also shown for comparison. Although the Coulomb-Born approximation provides accurate values for the high-l T-matrix elements which are needed for convergence, it grossly overestimates the low-l contributions. Thus the total cross section, particularly at low energies, is much too large. For high energies the error is reduced, but is still substantial.

Of the available experimental determinations of the $X \rightarrow B$ excitation cross section, our results are in good agreement with the results of Crandall *et al.*[4] Their values are also plotted in Fig. 1. Earlier crossed-beam experiments of Lee and Carleton[1] and Dashchenko, Zapesochnyi, and Imre,[3] though in qualitative agreement with one another, are significantly larger than the results of Crandall *et al.*, and even lie above our Coulomb-Born results for all energies considered here. The small differences between our theoretical cross sections and the measurements of Crandall *et al.* are most likely attributable in the error in our computed value for the $X \rightarrow B$ transition moment.

IV. CONCLUSIONS

We have outlined a modification of the complex Kohn variational method which is suitable for studying the scattering of electrons from molecular ions. We have also implemented a prescription for computing converged total cross sections for optically allowed transitions. We have illustrated this approach with a study of the electron impact excitation of the B state of N_2^+. These calculations took explicit account of coupling between the three lowest states of the ion. Our calculations have employed compact, correlated target wave function which are required to properly describe the $X \rightarrow B$ transition moment of N_2^+. When we combine the dynamically important, low-l components of the T matrix with asymptotic Coulomb-Born values for the higher ($l > 6$) partial wave T-matrix elements, we obtain total cross sections for the $X \rightarrow B$ transition which are in good agreement with the most recent experimental measurements.

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