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Electron-Excitation Cross Sections of Sodium by the Method of Close Coupling[*]

Dale F. Korff, Sunggi Chung, and Chun C. Lin
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

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The electron-excitation cross sections of the $3\,^2P$, $3\,^2D$, $4\,^2S$, $4\,^2P$, $4\,^2D$, and $4\,^2F$ states have been calculated at several incident energies between 4 and 24 eV by using the method of close coupling. Three different sets of calculations in which the wave functions of the electron-atom system are expanded by three states ($3s$, $3p$, $3d$), by seven states ($3s, 3p, 3d, 4s, 4p, 4d, 4f$), and by eight states ($3s, 3p, 3d, 4s, 4p, 4d, 4f, 5p$) of the target atom, have been performed in order to investigate how the cross sections are influenced by the indirect coupling of the ground state to the final state through the intermediate ones. The $3\,^2D$ cross sections are found to be about 30% higher than the values obtained by the Born approximation and by the scheme of $3s$-$3d$ two-state close coupling. The strong coupling of $3s$ with $3p$ and of $3d$ with $3p$ provides an indirect coupling between $3s$ and $3d$ which is mainly responsible for the large increase of the $3\,^2D$ cross sections over the Born-approximation values. A similar kind of increase in the cross sections is also observed for the $4\,^2D$ state owing to the indirect coupling through the intermediate $3p$ and $4p$ states. Inclusion of the intermediate states $3\,^2D$, $4\,^2D$, and $4\,^2S$ in the close-coupling calculation likewise affects considerably the $3\,^2P$ and $4\,^2P$ cross sections. The effect of indirect coupling is most pronounced in the $4\,^2F$ cross sections (ranging from a fourfold to a tenfold increase over the Born approximation), because the direct coupling between $3s$ and $4f$ is weak and of rather short range so that the major contribution to the cross sections arises from the indirect part. Comparisons of the theoretical cross sections with the experimental values are made.

I. INTRODUCTION

In the last decade a great deal of effort has been directed toward the experimental study of electron excitation of atoms. Excitation cross sections for a number of atoms have been measured and comparisons of the experimental data with theory have been made.[1] Many of the theoretical calculations of the cross sections were based on the Born approximation.[2] For some cases the Born theoretical cross sections are in rather good agreement with the experimental values at high energies, whereas in many other cases, notably for the dipole-forbidden states (with respect to the ground state), the Born approximation tends to underestimate the excitation cross sections.[3-5] In the case of neon and argon, the Born approximation (first) gives zero excitation cross sections for a number of non-spin-forbidden states for which quite substantial cross sections were observed experimentally at high energies.[6]

In performing a Born-approximation calculation of the excitation cross sections, one essentially makes two approximations, i.e., (i) considering the coupling of the final state with only the initial state and neglecting the roles of all the other excited states, and (ii) neglecting distortion and the back coupling from the final to the initial state (plane-wave approximation). The second approximation may be expected to be valid at high energies; indeed, high incident energy as a major criterion for the applicability of the Born approximation has been well recognized. However, the consequence of approximation (i) was not as fully appreciated until rather recently. For excitation to a dipole-allowed state, the interaction between the incident electron and the target atom provides a coupling of the final state of the atom with the initial state, which is usually strong enough so that omission of all other states may be justified. On the other hand, if the direct initial-final state coupling is relatively weak, as in many cases of the dipole-forbidden states, there may exist a third state which couples strongly to both the initial and final states. Such a state then provides an indirect coupling for the excitation process in question. The Born-approximation excitation cross sections would be in serious error if the indirect coupling becomes as important as the direct one. Thus at moderately high energy the Born approximation may give good excitation cross sections for the dipole-allowed states but becomes less satisfactory for the spin-allowed dipole-forbidden states. This indirect coupling effect was suggested as an explanation of the observation in helium that the Born cross sections agree reasonably well with experiment for the ^1P states but are much below the measured values in the case of the ^1D series, and calculations of the ^1D cross sections by means of the multistate close-coupling scheme have demonstrated quantitatively the importance of the indirect coupling.[7,8]

One way to take the indirect coupling into account is to go on to the second Born approximation which allows one to treat the indirect coupling via each intermediate state individually. However, the Born series does not necessarily converge unless the couplings are sufficiently weak. When the couplings of some of the intermediate states with the initial state and/or with the final state are strong, going to higher-order Born-type corrections does not always yield satisfactory results.

In this paper we adopt the method of close coupling to investigate quantitatively the effect of indirect coupling on the excitation cross sections. In addition to the initial and final states, we attempt to include as many intermediate states as is practical in setting up the scattering equations. Because the time required for the numerical computation increases drastically with the number of channels in the scattering problem, only a limited number of intermediate states can be covered. Selection of the intermediate states may be based on the strength of their coupling with the initial and final state. Thus for excitation of the $3\,^1D$ state of helium, we expect $2\,^1P$ and $3\,^1P$ to have a strong influence. Our calculations show that the indirect couplings via $2\,^1P$ and via $3\,^1P$ have an opposite effect on the cross section and tend to cancel each other quite substantially. An accurate calculation of the $3\,^1D$ cross section of helium would require a detailed examination of not only the $n=1, 2, 3, 4$ states but also possibly of some higher $n\,^1P$ states. A much better testing case is the $3\,^2D$ state of sodium. Here we can single out the $3\,^2P$ state as the most important intermediate state for furnishing an indirect coupling of the type $3\,^2S \to 3\,^2P \to 3\,^2D$, and the effect of $4\,^2P$ may be expected to be considerably smaller. For the case of sodium, the dipole matrix elements $(3s\,|\,z\,|\,np)$ and $(np\,|\,z\,|\,3d)$ become very small for $n \geq 5$ (the former being -2.505, -0.227, -0.083 a.u., and the latter being -3.043, 4.854, -0.080 a.u. for $n=3, 4, 5$, respectively), thus one may expect the results of a close-coupling calculation, which covers only the low excited states, to include adequately the effects of long-range polarization. With this in mind, we have performed a series of multistate close-coupling calculations for the electron excitation cross sections of the $3\,^2P$, $3\,^2D$, $4\,^2S$, $4\,^2P$, $4\,^2D$, and $4\,^2F$ states over the energy range of 4–23 eV and have analyzed the influence of the indirect coupling. It should be mentioned that the multistate close-coupling scheme has been used to calculate excitation cross sections for a number of atoms including H, He$^+$, Ca$^+$, and Mg$^+$.[9] Most of them, however, were confined to the near-threshold region so that some of the intermediate states included are closed channels. Our calculations, on the other hand, are conducted at much higher energies with all open-channel intermediate states.

While the Born approximation is generally adequate for excitation of dipole-allowed states at energies several times larger than the excitation energy, an exception to this rule is the case of the first resonant states of the alkali-metal atoms. It has been pointed out that the coupling between the $3\,^2S$ and $3\,^2P$ state of sodium is so strong that the Born approximation grossly overestimates the excitation cross section of $3\,^2P$ over a wide range of energy, and the use of two-state close coupling indeed gives much smaller cross sections.[10] In this paper we shall examine in more detail the cross sections of the $3\,^2P$ state by means of multistate close-coupling schemes. For excitation calculations of the sodium atom the method of close coupling is a particularly important tool, as the Born approximation tends to overestimate the cross sections of the $3\,^2P$ state and underestimate those of $n\,^2D$.

The majority of the calculations reported in this paper was done with the incident energy of the electron between 10 and 24 eV. In this energy range the kinetic energy of the incident electron is substantially larger than that of the valence electron. Except for the unusually strong-coupling case of $3\,^2P$ cited in the preceding paragraph, and for a low-energy point of $4\,^2S$, the use of the plane-wave approximation as done in the Born-type calculations of the total excitation cross sections gives satisfactory results in the range of 10–24 eV (see Sec. III). On the other hand, the effects of indirect coupling on the cross sections of the ^2D states prove to be very important. In some cases we have carried the calculations down to incident energies of 7.364 and 4.21 eV to examine the indirect coupling at lower energy. However, the cross sections at 4.21 eV are not expected to have the same accuracy as those at higher energies since the exchange of the incident and atomic electrons was neglected in this work. Extension of the calculations beyond 24 eV was not made, partly because we have already detected a trend of decreasing importance of the indirect-coupling effects with increasing energy, and partly because our close-coupling calculations at higher energy require the solutions of more partial waves and therefore entail more lengthy computations. We have, instead, confined ourselves to the "intermediate" energy range where the deviation of many of the excitation cross sections from their Born-approximation values is most pronounced.

II. FORMULATION AND SOLUTION OF SCATTERING EQUATIONS

The formulation of the problem of electron-atom excitation by the close-coupling scheme has been discussed extensively in the literature.[10,11] In this section we shall outline only the key steps which are essential in the subsequent discussion.

Let us denote the coordinates of the incident electron by $\vec{r}$ and those of the electrons of the atom (nuclear charge Z) by $\vec{r}_1, \vec{r}_2, \ldots$. The Hamiltonian (in Hartree's atomic units) divides naturally into that of the isolated atom, the kinetic energy of the incident electron, and the interaction between the incident electron and the atom, i.e.,

$$H = H_a - \tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \sum_i |\vec{r} - \vec{r}_i|^{-1} . \tag{1}$$

The wave functions of the free atom $\psi(nl_a m_a | \vec{r}_1, \vec{r}_2, \ldots)$, which are characterized by n and by the angular momentum quantum numbers $l_a m_a$, are compounded with the partial waves $Y_{lm}(\hat{r})$ of the incident electron by means of the Clebsch–Gordan coefficients to form the coupled-representation basis functions of total angular momentum (LM) as

$$\psi_\nu(\vec{r}_1, \vec{r}_2 \ldots, \hat{r}) = \sum_{m_a m} C^{l_a l L}_{m_a m M}\, \psi(nl_a m_a | \vec{r}_1, \vec{r}_2, \ldots) Y_{lm}(\hat{r}). \tag{2}$$

One then expands the wave function of the complete system in the form of

$$\Psi(\nu' | \vec{r}_1, \vec{r}_2, \ldots \vec{r}) = r^{-1} \sum_\nu F_\nu(\nu' | r) \psi_\nu(\vec{r}_1, \vec{r}_2, \ldots \hat{r}) . \tag{3}$$

In this paper we neglect the exchange of the incident electron with the atomic electrons. The functions $F_\nu(\nu' | r)$ are the solution of the set of coupled differential equations

$$\left(\frac{d^2}{dr^2} - \frac{l_\nu(l_\nu + 1)}{r^2} + k_\nu^2\right) F_\nu(\nu' | r) = \sum_\mu U_{\nu\mu}(r)\, F_\mu(\nu' | r) , \tag{4}$$

where

$$\begin{aligned} U_{\nu\mu}(r) &= 2\int \psi_\nu^*(\vec{r}_1, \vec{r}_2 \ldots \hat{r}) \left(-\frac{Z}{r} + \sum_i |\vec{r} - \vec{r}_i|^{-1}\right) \\ &\qquad \times \psi_\mu(\vec{r}_1, \vec{r}_2, \ldots \hat{r})\, d\vec{r}_1\, d\vec{r}_2 \ldots d\hat{r} \\ &= 2 \sum_{m_a m m'_a m'} C^{l_a l L}_{m_a m M} C^{l'_a l' L}_{m'_a m' M} \int Y^*_{lm}(\hat{r}) \\ &\qquad \times V_{nl_a m_a, n' l'_a m'_a}(\vec{r}) Y_{l'm'}(\hat{r})\, d\hat{r} , \end{aligned} \tag{5}$$

$$\begin{aligned} V_{nl_a m_a, n' l'_a m'_a}(\vec{r}) = \int & \psi^*(nl_a m_a | \vec{r}_1, \vec{r}_2 \ldots) \\ & \times \left(-\frac{Z}{r} + \sum_i |\vec{r} - \vec{r}_i|^{-1}\right) \\ & \times \psi(n' l'_a m'_a | \vec{r}_1, \vec{r}_2 \ldots)\, d\vec{r}_1\, d\vec{r}_2 \ldots , \end{aligned} \tag{6}$$

with the asymptotic condition either in terms of the S matrix as

$$F_\nu^S(\nu' | r) \sim k^{-1/2} \left(e^{-i(kr - l\pi/2)} \delta_{\nu\nu'} - e^{i(kr - l\pi/2)} S_{\nu\nu'}\right), \tag{7}$$

or in terms of the R matrix as

$$F_\nu^R(\nu' | r) \sim k^{-1/2} \left[\sin(kr - \tfrac{1}{2} l\pi) \delta_{\nu\nu'} + \cos(kr - \tfrac{1}{2} l\pi) R_{\nu\nu'}\right] . \tag{8}$$

From the R-matrix elements, the excitation cross sections can be computed in the usual manner.[10]

To render the solution of the coupled differential equations tractable, several approximations were introduced. The number of terms included in the expansion of Eq. (3) must be limited to a manageable size. Selections of the atomic states in the close-coupling manifold will be discussed in detail in Sec. III. The wave functions of the free atom are approximated by antisymmetrized products of one-electron orbitals ϕ determined by the Hartree–Fock–Slater self-consistent-field procedure.[12] The coefficient of the Slater exchange potential is adjusted to give good agreement between the calculated valence-electron energy and the experimental value. The 4*s* function obtained in this manner is not automatically orthogonal to 3*s*; thus it is necessary to orthogonalize the 4*s* function to 3*s*, and 4*p* to 3*p*, etc. In this work we confine ourselves to the singly excited configuration like $1s^2 2s^2 2p^6 nl_a$ for sodium. The interaction potential matrix elements of Eq. (6) are to be evaluated between the $|\phi_{1s} \ldots \phi_{2p} \phi_{nl_a}|$ and $|\phi'_{1s} \ldots \phi'_{2p} \phi_{n'l'_a}|$ configurations. Although in principle the core-state functions in the two different configurations are different as denoted by ϕ_i and ϕ'_i ($i = 1s, 2s, 2p$), the numerical values of the overlap integrals of the corresponding orbitals $\langle \phi_i | \phi'_i \rangle$ are very close to unity (typically 0.9988), and the integrals $\langle \phi_i | \phi'_j \rangle$ with $i \neq j$ are no greater than the order of 10^{-2}. Hence in computing the nondiagonal elements of the interaction potential, we neglect the difference between the set of ϕ_i and ϕ'_i and obtain

$$V_{nl_a m_a, n' l'_a m'_a}(r) = \int \phi^*_{nl_a m_a}(\vec{r}_1)\, |\vec{r} - \vec{r}_1|^{-1}\, \phi_{n' l'_a m'_a}(\vec{r}_1)\, d\vec{r}_1 . \tag{9}$$

The diagonal part likewise can be reduced to

$$\begin{aligned} V_{nl_a m_a, nl_a m_a}(\vec{r}) = \frac{-11}{r} &+ \sum_i \int \phi_i(\vec{r}_1)\, |\vec{r} - \vec{r}_1|^{-1} \phi_i(\vec{r}_1)\, d\vec{r}_1 \\ &+ \int \phi_{nl_a m_a}(\vec{r}_1)\, |\vec{r} - \vec{r}_1|^{-1}\, \phi_{nl_a m_a}(\vec{r}_1)\, d\vec{r}_1 . \end{aligned} \tag{10}$$

The second member of the above expression (which is to be summed over all ten core electrons) represents the interaction of the incident electron with the $1s^2 2s^2 2p^6$ core. Since the core electrons extend only over a small domain near the nucleus, we ignore the structure of the core and thus replace each integral inside the summation by $1/r$. (The effect of the core size will be discussed in Sec. IV.) Equation (10) then becomes

$$V_{nl_a m_a, nl_a m_a}(\vec{r}) = -\frac{1}{r} + \langle \phi_{nl_a m_a}(\vec{r}_1) \left| \frac{1}{|\vec{r} - \vec{r}_1|} \right| \phi_{nl_a m_a}(\vec{r}_1) \rangle , \quad (11)$$

which is essentially the expression for a one-electron atom.

With a given selection of the target states in the close-coupling expansion (e.g., $3s$, $3p$, $3d$) and for a given L and M we set up the scattering equations (which are independent of M) in accordance with Eq. (4). The values of the angular momentum of the partial waves (l) range from $L + l_a$ to $|L - l_a|$. The nondiagonal interaction potential $U_{\mu\nu}(r)$ between a channel of even value of $l_a + l$ and one with odd $l_a + l$ vanishes, thus the system of the scattering equations separates into two subsets. For example, inclusion of the atomic states $3s$, $3p$, $3d$, $4s$, $4p$, $4d$, and $4f$ results in a set of 16-channel and a set of 9-channel equations for $L \geq 3$.

The numerical procedure for solving the coupled differential equation system of Eq. (4) has been described previously.[10,13] The solution is initiated near the origin by a Frobenius-type expansion and developed out from the origin using a Numerov method.[14] With a series of transformations as outlined in Ref. 10, the solution is then matched to the asymptotic form of Eq. (8) in order to obtain the R-matrix elements. In matching the solution to the desired asymptotic form, it is more expedient to use the spherical Bessel and Neumann functions in place of the sine and cosine functions. Since some of the nondiagonal members of $U_{\nu\mu}(r)$ have a very long range like r^{-2}, we have found it necessary in some cases to carry the numerical integration of the differential equations to a distance of $200a_0$, where a_0 is the Bohr radius, before matching the solutions to the appropriate asymptotic forms. The computations then become exceedingly time consuming when a large number of channels are included. Burke and Schey[11] have given a method to get around this difficulty using an asymptotic expansion. This method works well for the case where only the $3s$, $3p$, and $3d$ states are included in the expansion of Eq. (3). For this $3s$-$3p$-$3d$ problem, numerical integration up to $r = 80a_0$ gives R-matrix elements good to about 1%. However, when the states with $n = 4$ are added to the manifold of the expansion, complications arise because the small energy separations of some of the channels ($4p$ and $3d$) cause poor convergence of the asymptotic expansion. We have therefore introduced an alternative scheme for obtaining the R matrix without having to carry out the numerical solution to an unduly large distance. This scheme is described briefly in the following paragraph.

Let us write the solution $\underline{F}$ which has the asymptotic properties of Eq. (8) in a matrix form so that $F_{\nu\nu'}(r)$ corresponds to $F_\nu^R(\nu' | r)$, and likewise the interaction potential $U_{\mu\nu}(r)$ as a matrix $\underline{U}(r)$. The solution of the scattering equation which conforms to the R-matrix-type asymptotic form may be written in terms of the homogeneous solution [spherical Bessel function $j(r)$ and spherical Neumann function $n(r)$] as

$$\underline{F}(r) = \underline{J}(r)\, \underline{X}(r) + \underline{N}(r)\, \underline{Z}(r) , \quad (12)$$

where

$$J_{ij}(r) = k_i^{1/2} r\, j_{l_i}(k_i r) \delta_{ij} , \quad (13)$$

$$N_{ij}(r) = -k_i^{1/2} r\, n_{l_i}(k_i r) \delta_{ij} , \quad (14)$$

$$\underline{X}(r) = \underline{1} - \int_r^\infty \underline{N}(s) \underline{U}(s) \underline{F}(s)\, ds , \quad (15)$$

$$\underline{Z}(r) = \underline{R} + \int_r^\infty \underline{J}(s) \underline{U}(s) \underline{F}(s)\, ds , \quad (16)$$

$$\underline{R} = -\int_0^\infty \underline{J}(s) \underline{U}(s) \underline{F}(s)\, ds . \quad (17)$$

By examining the asymptotic behavior of Eq. (12), it is easy to show that the quantity defined in Eq. (17) is indeed the same as the R matrix introduced earlier. Differentiation of Eq. (12) along with the use of Eqs. (15) and (16) gives

$$\frac{d}{dr} \underline{F}(r) = \left(\frac{d}{dr} \underline{J}(r) \right) \underline{X}(r) + \left(\frac{d}{dr} \underline{N}(r) \right) \underline{Z}(r) . \quad (18)$$

As $\underline{F}(r)$ and $d\underline{F}(r)/dr$ can be determined by numerical integration, and $\underline{J}(r)$ and $\underline{N}(r)$, as well as their derivatives, are readily available, one can evaluate $\underline{X}(r)$ and $\underline{Z}(r)$ at any point. It is convenient to define

$$\underline{\hat{R}}(r) \equiv \underline{Z}(r) \underline{X}^{-1}(r) = \left[\underline{R} + \int_r^\infty \underline{J}(s) \underline{U}(s) \underline{F}(s)\, ds \right] \times \left[\underline{1} - \int_r^\infty \underline{N}(s) \underline{U}(s) \underline{F}(s)\, ds \right]^{-1} \quad (19)$$

which reduces to the R matrix when r tends to infinity.

If we fix r to be some value r_m where we may expect $\underline{\hat{R}}(r_m)$ to be approximately equal to $\underline{R}$, then Eqs. (12), (15), (16), and (19) can be used as the basis for an iterative approach. As the zeroth-order approximation we take

$$\underline{R}^{(0)} = \underline{\hat{R}}(r_m) , \quad (20)$$

$$\underline{F}^{(0)}(r) = \underline{J}(r) + \underline{N}(r) \underline{R}^{(0)} , \quad r > r_m . \quad (21)$$

An improved version of $\underline{R}$ (designated as $\underline{R}^{(1)}$) is then obtained by putting $\underline{F}^{(0)}(r)$ back into Eq. (19):

$$\underline{R}^{(0)} = \left[\underline{R}^{(1)} + \int_{r_m}^\infty \underline{J}(s) \underline{U}(s) \underline{F}^{(0)}(s)\, ds \right]$$

$$\times[\underline{1} - \int_{r_m}^{\infty} \underline{N}(s)\underline{U}(s)\underline{F}^{(0)}(s)\,ds]^{-1}\,, \qquad (22)$$

and $\underline{F}^{(1)}$ is obtained from Eq. (12) with $\underline{X}(r)$ and $\underline{Z}(r)$ computed by the approximation of substituting $\underline{F}^{(0)}(s)$ and $\underline{R}^{(1)}$ for $\underline{F}(s)$ and $\underline{R}$, respectively, in Eqs. (15) and (16). Although this scheme can be repeated to achieve higher-order approximations, the computational procedure becomes quite lengthy beyond Eq. (22). Nevertheless, even with a single iteration, this method still proves to be very useful. Test calculations performed for some selected partial waves of the $3s$-$3p$-$3d$ and the $3s$-$3p$-$3d$-$4p$ problem show that the cross sections obtained from $\underline{R}^{(1)}$ with matching at $r_m = 60a_0$ are generally accurate to within 1%. In fact, even a matching point at as low as $40a_0$ is found to be quite satisfactory (~ 2%).

For each incident energy the scattering equations were solved from $L = 0$ to typically $L = 16$. A plot of the log of the partial-wave cross sections versus L is nearly a straight line for large L. Cross sections for $L > 16$ were obtained by extrapolation of this plot. To check the accuracy of this procedure, we have computed the partial-wave cross sections for selected high L values at 16.8 and 23.1 eV with the $3s$-$3p$-$3d$ close-coupling scheme, and the results agree with the extrapolated values to within 10% for $L = 20$ and 24 at both energies.

III. RESULTS

A. Excitation Cross Sections of $3\,^2P$

The problem of electron excitation of the $3\,^2P$ state of sodium has been treated by several authors.[10,15,16] Because of the unusually strong coupling between the $3s$ and the $3p$ state produced by the interaction between the incident electron and the sodium atom, the use of the Born approximation results in a very serious overestimation of the excitation cross sections. To correct for this overestimation, Seaton[15] has given modified versions of the Born approximation which preserve the unitary property of the S matrix. Barnes, Lane, and Lin[10] performed two-state $3s$-$3p$ close-coupling calculations (neglecting exchange between the incident and the atomic electron) for five energies between 4.2 and 23.1 eV. In the two-state close-coupling calculations of Karule and Peterkop[16] which cover the energy region from threshold to 5 eV, allowance was made for the exchange effect. Compared to the results of the Born approximation, all of the more refined calculations cited above yield considerably smaller cross sections of the $3\,^2P$ state.

We have calculated the excitation cross sections of the $3\,^2P$ state by taking three different sets of atomic states in the close-coupling expansion, i.e., $3s$-$3p$, $3s$-$3p$-$3d$, and $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$. The results are summarized in Fig. 1. Our $3\,^2P$ cross sections of the $3s$-$3p$ two-state calculations are about 10% lower than the values obtained by Barnes, Lane, and Lin.[10] The difference in cross sections is due to the different choice of wave functions, i.e., Barnes *et al.* used for the valence electron of the sodium atom hydrogen-like wave functions (with an effective charge adjusted to fit the experimental $3s$-$3p$ line strength), whereas the atomic electrons are represented by the Hartree–Fock–Slater wave functions in this work. The $3\,^2P$ cross sections become smaller when the $3d$ atomic state is added to the manifold of the scattering equations. The radial integral $(3p|r|3d)$ is of comparable magnitude to $(3s|r|3p)$, thus the $3p$-$3d$ coupling terms "channeled" the $3s$-$3p$ coupling to the $3d$ state, resulting in a decrease of the $3^2S \to 3^2P$ excitation cross sections and simultaneously an increase of the $3^2S \to 3^2D$ cross sections (see Sec. III B) from their respective two-state close-coupling values. The coupling of the $3p$ state with the $4d$ state is much weaker than the $3p$-$3s$ and $3p$-$3d$ pairs; hence the $3\,^2P$ cross sections are reduced only slightly in going from the $3s$-$3p$-$3d$ to the seven-state manifold. The very small difference between the three-state and seven-state results suggests that we have reached good convergence in the multistate expansion as far as the $3\,^2P$ cross sections are concerned. A listing of the partial-wave cross sections of the two-, three-, and seven-state calculations for a few energies is given in Table I. The indirect coupling via the $3d$ state is seen to be effective in decreasing the $3\,^2P$ partial-wave cross sections from their two-state values over the entire range of partial waves shown, while the indirect coupling via the $n = 4$ states is effective only at low and intermediate partial waves. Also shown in Fig. 1 are two sets

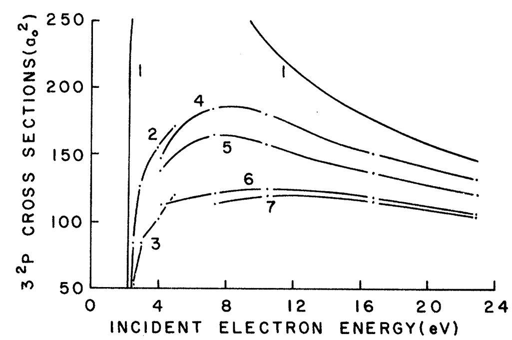

FIG. 1. Electron-excitation cross sections of the $3\,^2P$ state of sodium calculated by the first Born approximation (1), two-state $3s$-$3p$ close coupling without core and exchange (5), three-state $3s$-$3p$-$3d$ close coupling without core and exchange (6), seven-state $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close coupling without core and exchange (7). The other cross sections shown are the two-state $3s$-$3p$ close-coupling results of Karule and Peterkop (2, with core and without exchange; 3, with core and exchange) and of Barnes, Lane, and Lin (4, without core and exchange).

TABLE I. Partial-wave excitation cross sections of the $3\,^2P$ state of sodium.[a]

	Q_L in units of a_0^2											
	E = 7.364 eV			E = 10.520 eV			E = 16.832 eV			E = 23.144 eV		
L	2-st	3-st	7-st	2-st	3-st	7-st	2-st	3-st	7-st	2-st	3-st	7-st
0	5.27	3.18	2.67	3.24	2.04	1.90	1.43	1.02	1.06	0.75	0.56	0.61
1	3.44	1.63	2.46	2.26	1.04	1.44	0.87	0.47	0.66	0.41	0.24	0.34
2	9.06	5.75	5.27	3.64	2.38	2.51	1.12	0.71	0.89	0.51	0.32	0.44
3	29.02	23.10	18.87	15.59	12.57	11.26	5.57	4.62	4.50	2.56	2.16	2.19
4	28.24	20.22	16.22	20.17	17.15	15.11	9.58	8.55	8.10	5.05	4.57	4.46
5	22.92	13.03	12.34	19.54	14.93	13.37	11.44	10.26	9.63	6.83	6.32	6.09
6	17.65	11.27	11.45	17.19	12.09	11.44	11.72	10.17	9.57	7.71	7.12	6.83
7	13.24	9.86	10.07	14.60	10.23	10.12	11.13	9.34	8.89	7.91	7.19	6.90
8	9.79	8.07	8.23	11.98	8.93	8.95	10.18	8.37	8.09	7.69	6.86	6.62
9	7.17	6.28	6.40	9.84	7.76	7.78	9.11	7.48	7.33	7.24	6.38	6.18
10	5.21	4.74	4.85	7.93	6.59	6.62	8.07	6.69	6.62	6.69	5.86	5.72
11	3.76	3.52	3.60	6.40	5.50	5.54	7.10	6.00	5.96	6.12	5.38	5.27
12	2.71	2.58	2.65	5.15	4.58	4.58	6.22	5.35	5.34	5.57	4.90	4.84
13	1.95	1.87	1.92	4.15	3.73	3.73	5.43	4.78	4.78	5.04	4.49	4.45
14	1.40	1.35	1.40	3.31	3.07	3.06	4.74	4.24	4.23	4.56	4.09	4.06
15							4.14	3.76	3.75	4.12	3.73	3.70
16							3.16	3.32	3.30	3.72	3.41	3.38

[a] 2-st, 3-st, and 7-st mean $3s$-$3p$, $3s$-$3p$-$3d$, and $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close coupling, respectively.

of two-state close-coupling cross sections of the $3\,^2P$ state given by Karule and Peterkop, one with both the exchange and core effects included and the other containing core effects only without exchange. McCavert and Rudge[17] have calculated excitation cross sections for several states of Na. In their calculations, a plane-wave approximation in a modified form was used. Because of the basic difference between their approach and ours, no comparison of these two sets of results will be made.

A comparison of our calculations with experiments is illustrated in Fig. 2. Measurements of the excitation function of the $3\,^2P \rightarrow 3\,^2S$ transition have been reported by Zapesochnyi and Shimon.[18] Zapesochnyi[19] subsequently has given an absolute excitation function of the $3\,^2P$ state (with cascade correction). It was pointed out, however, by Moiseiwitsch and Smith[1] that the cross sections of Ref. 18 may possibly be too low. The cross sections given by Enemark and Gallagher[20] were obtained by normalizing their optical measurements to the Born-approximation value at 1000 eV. Our theoretical cross sections (seven-state calculation) are considerably higher than the values given by Zapesochnyi, but are in very good agreement with the results of Enemark and Gallagher. The measurements reported by Christoph[21] in 1935 are much higher than our seven-state cross sections. Further experimental work on absolute excitation cross sections should be particularly valuable for testing the theory.

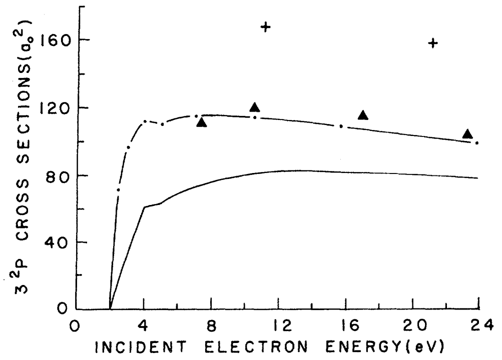

FIG. 2. Comparison of the electron-excitation cross sections of the $3\,^2P$ state of sodium calculated by seven-state $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close coupling without core and exchange (▲) with the experimental results of Enemark and Gallagher (dash-dots), Zapesochnyi (solid curve), and Christoph (+).

B. Excitation Cross Sections of $3\,^2D$

We have calculated the electron-excitation cross sections of the $3\,^2D$ state by using the Born approximation, a two-state ($3s$-$3d$), a three-state ($3s$-$3p$-$3d$), and a seven-state (n = 3, 4) close-coupling scheme. The results are displayed in Fig. 3. For the $3\,^2D$ state as well as $4\,^2S$, $4\,^2P$, and $4\,^2D$, the Born cross sections computed in this work agree with those given by Vainshtein[22] to within typically 2–4%. The $3s$-$3d$ coupling is much weaker than the $3s$-$3p$; as a result the gross overestimation of the excitation cross sections by the Born approximation discussed in Sec. III A is absent here. In fact the good agreement between the two-state close-coupling and the Born-approximation cross sections supports the validity of the plane-wave

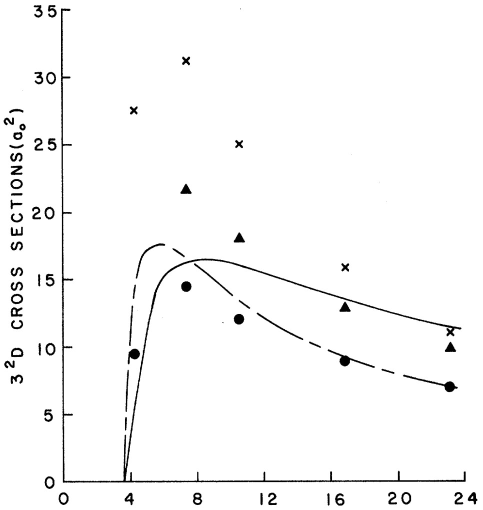

FIG. 3. Electron-excitation cross sections of the $3\,^2D$ state of sodium calculated by the first Born approximation (long-short dashes), two-state $3s$-$3d$ close coupling without core and exchange (●), three-state $3s$-$3p$-$3d$ close coupling without core and exchange (×), and seven-state $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close coupling without core and exchange (▲). The optical excitation function of the $3\,^2D$-$3\,^2P$ transition measured by Zapesochnyi and Shimon (solid curve) is also shown.

approximation for the $3\,^2D$ excitation in the "intermediate" energy range. On the other hand, since both the $3s$-$3p$ and the $3p$-$3d$ coupling are strong, their cumulative effect is to produce an indirect coupling between $3s$ and $3d$ which may be of comparable strength to the direct $3s$-$3d$ coupling. This is reflected by the large increase of the theoretical cross sections in going from the two-state to the three-state calculation.

It is interesting to note that the inclusion of the $n=4$ states substantially reduces the cross sections from the values of the three-state calculations. Of the four members of the $n=4$ group, the $4\,^2P$ state may be expected to be mainly responsible for these reductions. In other words, the effect of the indirect coupling $3s \rightarrow 4p \rightarrow 3d$ cancels an appreciable part of the $3s \rightarrow 3p \rightarrow 3d$. A similar kind of cancellation, though to a much less extent, is found in the matrix elements of z^2, i.e.,

$$\langle 3s\,|z^2|\,3d\rangle = \sum_n \langle 3s\,|z\,|np\rangle\langle np\,|z\,|3d\rangle \;. \qquad (23)$$

Numerical computations by means of the Hartree-Fock-Slater wave functions give $\langle 3s\,|z^2|\,3d\rangle$, $\langle 3s\,|z\,|\,3p\rangle\langle 3p\,|z\,|\,3d\rangle$, $\langle 3s\,|z\,|\,4p\rangle\langle 4p\,|z\,|\,3d\rangle$, and $\langle 3s\,|z\,|\,5p\rangle\langle 5p\,|z\,|\,3d\rangle$ as 6.527, 7.621, −1.104, and 0.007 a.u., respectively. The $4p$ state does tend to cancel part of the $3p$ contribution in the right-hand side of Eq. (23), while the contribution from the $5p$ state is insignificant. Motivated by this observation, we have added the $5p$ state to the $n=3$ and $n=4$ states, and calculated the $3\,^2D$ cross section at 10.5 and 16.8 eV with this eight-state manifold. The cross sections are $19.4a_0^2$ and $13.5a_0^2$, being 5.6 and 2.8%, respectively, above the seven-state result. The small difference here indicates that the close-coupling method is also converging rather well for the $3\,^2D$ case.

In Table II are given the $3\,^2D$ partial-wave cross sections. In comparing the two- and three-state partial waves, the effect of the $3p$ state in increasing the $3\,^2D$ cross sections is seen to occur for almost all of the partial waves. Similarly, in going from the three- to seven-state calculation, the effect of the $n=4$ states in decreasing the $3\,^2D$ cross section is evident for nearly all the partial waves except those of large L for which the seven-state results appear to be converging rather well to the three-state ones.

The experimental data of the optical excitation function of the $3^2D \rightarrow 3^2P$ transition observed by Zapesochnyi and Shimon[18] are included in Fig. 3 for comparison with the theoretical calculations. To estimate the amount of cascade into the $3\,^2D$ level, we note that the contribution from the $n\,^2P$ states is negligible because of the very small probability of the $n\,^2P \rightarrow 3\,^2D$ transitions in comparison with the $n\,^2P \rightarrow n'\,^2S$. From our calculated cross sections of the $4\,^2F$ state (Sec. III E), we estimate that the $4\,^2F \rightarrow 3\,^2D$ cascade contribution is about 10% above 10 eV but may become higher at lower energies. In the absence of a detailed cascade analysis, we shall not apply the cascade corrections to the optical excitation data of Zapesochnyi and Shimon which were estimated to have an accuracy of about 30–35%. Our cross sections calculated by the seven-state close-coupling scheme agree well with the observed values at 16.8 and 23.1 eV, but a much larger discrepancy is seen at 7.36 eV. Because of the omission of exchange in the calculations, our cross sections at 4.2 eV are expected to be of lower accuracy than the ones at higher energies. The Born-approximation cross sections are substantially lower than the experimental ones except at very low energies.

C. Excitation Cross Sections of $4\,^2P$

The $3s$-$4p$ coupling is much weaker than the $3s$-$3p$ coupling; for this reason one may expect a better agreement between the Born approximation and the two-state close coupling for the $4\,^2P$ state than for $3\,^2P$. This is indeed borne out by our calculations as shown in Fig. 4. The two-state cross sections are somewhat below (~15%) the Born-approximation values whereas the seven-state calculations move the cross sections up by 15-25%. Inspection of the individual partial waves shows also only small variations in most of the partial cross

TABLE II. Partial-wave excitation cross sections of the $3\,^2D$ state of sodium.[a]

	Q_L in units of a_0^2											
	E=7.364 eV			E=10.520 eV			E=16.832 eV			E=23.144 eV		
L	2-st	3-st	7-st	2-st	3-st	7-st	2-st	3-st	7-st	2-st	3-st	7-st
0	0.02	1.87	0.16	0.04	0.92	0.08	0.04	0.33	0.05	0.04	0.16	0.04
1	1.23	0.58	0.70	0.80	0.71	0.30	0.42	0.41	0.17	0.26	0.24	0.14
2	2.65	4.52	2.82	1.41	2.05	1.62	0.66	0.88	0.75	0.40	0.51	0.45
3	1.66	4.54	2.93	1.51	2.86	1.60	0.83	1.20	0.78	0.51	0.65	0.49
4	2.03	5.63	4.98	0.89	2.67	2.34	0.60	1.16	0.85	0.43	0.65	0.49
5	3.11	6.37	4.43	1.59	3.66	3.09	0.58	1.32	1.14	0.37	0.68	0.57
6	1.91	3.91	2.63	1.83	3.68	2.88	0.77	1.58	1.40	0.41	0.79	0.70
7	0.95	1.99	1.33	1.60	2.87	2.18	0.90	1.69	1.46	0.49	0.89	0.81
8	0.47	0.97	0.68	1.02	1.98	1.48	0.88	1.58	1.34	0.55	0.94	0.85
9	0.23	0.47	0.36	0.66	1.28	0.97	0.76	1.36	1.13	0.55	0.92	0.81
10	0.12	0.23	0.19	0.43	0.81	0.63	0.63	1.09	0.91	0.52	0.84	0.73
11		0.11	0.10	0.28	0.51	0.41	0.51	0.85	0.71	0.46	0.73	0.64
12		0.06	0.05	0.18	0.32	0.27	0.38	0.65	0.55	0.39	0.62	0.54
13		0.03	0.03	0.12	0.20	0.16	0.30	0.49	0.42	0.33	0.52	0.44
14		0.01	0.01	0.08	0.13	0.11	0.22	0.37	0.32	0.27	0.42	0.37
15							0.17	0.28	0.25	0.22	0.34	0.30
16							0.13	0.21	0.19	0.18	0.28	0.25

[a] 2-st, 3-st, and 7-st mean $3s$-$3d$, $3s$-$3p$-$3d$, and $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close coupling, respectively.

sections between the two-state and seven-state calculations. It may be noted in passing that for the $3\,^1P$ and $4\,^1P$ states of helium one finds only small differences among the excitation cross sections by the Born approximation, by the two-state, and by the multistate close-coupling scheme.[7,8]

Zapesochnyi and Shimon have measured the optical excitation cross sections of the $4\,^2P \rightarrow 3\,^2S$ transition.[18] By combining their data with the theoretical transition probabilities of the $4\,^2P \rightarrow 3\,^2S$, $4\,^2P \rightarrow 4\,^2S$, and $4\,^2P \rightarrow 3\,^2D$ lines calculated from the Hartree–Fock–Slater wave functions, we can deduce an excitation function of the $4\,^2P$ state which is labeled as "experimental" in Fig. 4. Since the $4\,^2P \rightarrow 4\,^2S$ transition is much stronger than the $4\,^2P \rightarrow 3\,^2S$, the "experimental" cross sections are quite sensitive to the errors of the theoretical transition probability of $4\,^2P \rightarrow 4\,^2S$. Furthermore, no attempt was made to correct for the cascade contribution. Nevertheless, the "experimental" cross sections seem to be much smaller than the theoretical cross sections (computed both by the Born approximation and by the close-coupling schemes) in addition to a very substantial difference in the shape of the excitation function.

D. Excitation Cross Sections of $4\,^2D$ and $4\,^2F$

Similar to the case of $3\,^2D$, the two-state close-coupling and the Born approximation give nearly

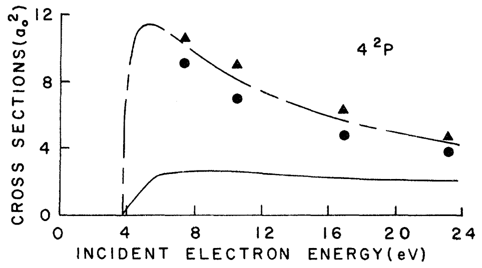

FIG. 4. Electron-excitation cross sections of the $4\,^2P$ state of sodium calculated by the first Born approximation (long-short dashes), two-state $3s$-$4s$ close coupling without core and exchange (●), and seven-state $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close coupling without core and exchange (▲). The "experimental" (see text) results of Zapesochnyi and Shimon (solid curve) are also shown.

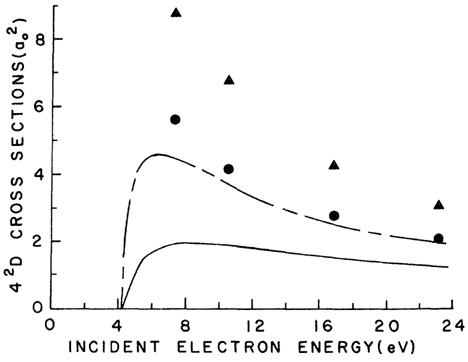

FIG. 5. Electron-excitation cross sections of the $4\,^2D$ state of sodium calculated by the first Born approximation (long-short dashes), two-state $3s$-$4d$ close coupling without core and exchange (●), and seven-state $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close coupling without core and exchange (▲). The "experimental" (see text) results of Zapesochnyi and Shimon (solid curve) are also shown.

identical cross sections for the 4^2D and 4^2F states (see Figs. 5 and 6). The very substantial deviation of the seven-state cross sections of 4^2D from the Born values as shown in Fig. 5 indicates the importance of indirect coupling in the excitation calculations. The major part of the indirect coupling may be expected to come from $3s \rightarrow 3p \rightarrow 4d$ and $3s \rightarrow 4p \rightarrow 4d$ which are included in the seven-state scheme. To ascertain the effect of the indirect coupling through the $5p$ state, we may note that upon adding $5p$ to the close-coupling manifold of the $n = 3$ and $n = 4$ states, the resulting eight-state scheme gives the cross sections of 4^2D at 10.5 and 16.8 eV as $5.7a_0^2$ and $3.6a_0^2$ as compared to the seven-state values of $6.8a_0^2$ and $4.4a_0^2$, respectively. The coupling of the $4d$ state with the np states becomes much weaker for $n > 5$. For this reason we expect the higher ^2P states to have only minor effects on the 4^2D cross sections. However, we have performed no calculations to verify this point as the inclusion of the higher states would make the solution of the scattering equations exceedingly time consuming.

The role of indirect coupling becomes even more remarkable in the excitation of the 4^2F state. Comparing our calculated cross sections based on the Born approximation and on the seven-state close-coupling scheme in Fig. 6, it is clear that the indirect coupling completely dominates the direct one over the energy region of our calculations. This striking feature is due to the fact that the direct coupling between $3s$ and $4f$ is weak and of rather short range (r^{-4} dependence at large distance). Our eight-state ($n = 3$, 4, and $5p$) calculation yields $2.7a_0^2$ and $1.2a_0^2$ as the 4^2F cross sections at 10.5 and 16.8 eV, respectively. Because of the relatively large number of intermediate states which may be important in the indirect coupling mechanism, no systematic investigation of the convergence behavior of the 4^2F cross sections has been made.

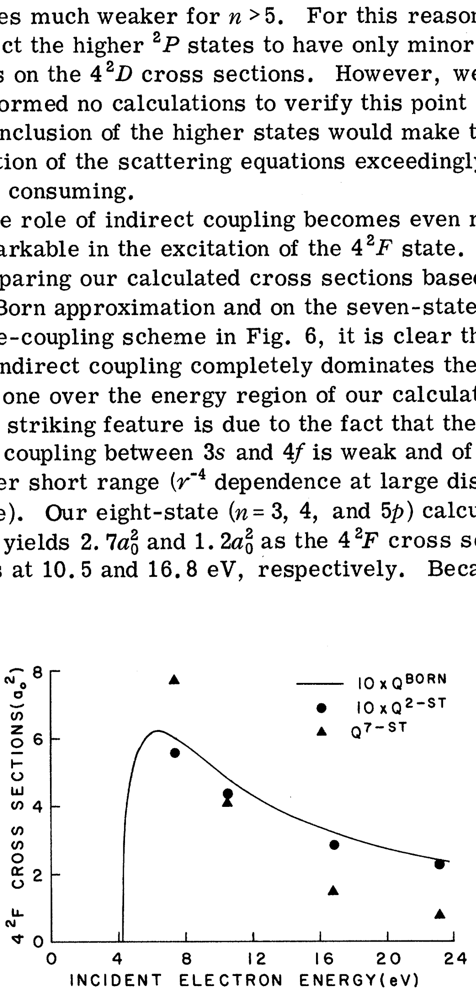

FIG. 6. Electron-excitation cross sections of the 4^2F state of sodium. The solid curve and the ● symbol give ten times the values of the cross sections calculated by the first Born approximation and ten times the two-state close-coupling values (without core and exchange), respectively. The seven-state $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close-coupling cross sections (without core and exchange) are represented by ▲.

Analogous to the 4^2P case, we have used theoretical transition probabilities to convert the optical cross sections of the $4^2D \rightarrow 3^2P$ transitions observed by Zapesochnyi and Shimon[18] into "experimental" excitation cross sections of the 4^2D state. These values (shown in Fig. 5) are much lower than both the Born-type and close-coupling theoretical cross sections.

E. Excitation Cross Sections of $4\,^2S$

In Fig. 7 are shown the 4^2S cross sections calculated by the Born approximation and by three different close-coupling schemes. Unlike the cases of 3^2D, 4^2D, and 4^2F, the two-state close-coupling scheme gives appreciably larger 4^2S cross sections than does the Born approximation. The difference may be due to the $3s$ distortion term, the $4s$ distortion, and/or the $4s$-$3s$ back coupling. Upon performing some test calculations, it was found that the $3s$ and $4s$ distortion terms are mainly responsible for the increase of the cross sections over the Born values. The results of the three-state close-coupling ($3s$-$3p$-$4s$) calculations indicate the importance of the indirect coupling through $3p$ on the 4^2S cross sections. The close agreement between the seven-state and the Born results is, of course, fortuitous, as the indirect coupling and distortion effects which are neglected in the Born approximation just counterbalance each other.

For the 4^2S state it is especially instructive to analyze the partial-wave cross sections given in Table III. The $3s$-$4s$ coupling is a short-range one, thus in the two-state calculation one would expect only the lower partial waves to contribute significantly to the total cross sections. Indeed, Table III shows that in the two-state case practically all of the total cross section comes from partial waves of $L = 0$ to $L = 4$. In going to the three-state case, the $3p$ state provides an indirect coupling between $3s$ and $4s$ which is of longer range than the direct coupling, with the result of increasing the higher partial-wave cross sections. However, as may be seen in Table III, there is a simultaneous reduction of the contributions from the partial waves of $L \leq 4$, and the reduction more than compensates for the gain in the large partial waves. Comparing the three-state to the seven-state calculations, we notice both increases and decreases in the partial-wave cross sections although the total cross sections remain nearly the same. This is in contrast with the 3^2D case where the inclusion of the $n = 4$ states tends to reduce practically all the partial-wave cross sections.

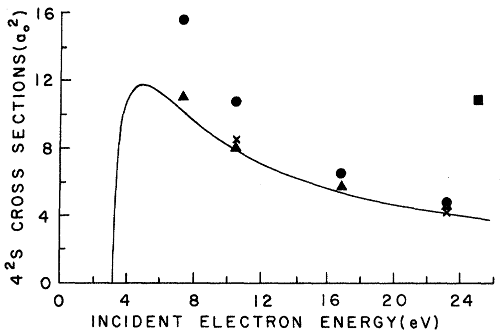

FIG. 7. Electron-excitation cross sections of the $4\,^2S$ state of sodium calculated by the first Born approximation (solid curve), two-state $3s$-$4s$ close coupling without core and exchange (●), three-state $3s$-$3p$-$4s$ close coupling without core and exchange (×), and seven-state $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close coupling without core and exchange (▲). Also shown is the result of Hertel and Rost (■) obtained by a second Born-type scheme.

A second Born-type scheme has been employed by Hertel and Rost[23] to calculate the $4\,^2S$ cross sections. The states included by these authors are $3s$, $4s$, and $3p$. Their value (see Fig. 7) at 25 eV is seen to be an overestimation by a considerable amount. The coupling largely responsible for the increase of the second Born over the first Born value was found to be the indirect $3s \rightarrow 3p \rightarrow 4s$ coupling. It is true that as far as the high-L partial waves are concerned, the $3s \rightarrow 3p \rightarrow 4s$ indirect coupling does have the effect of increasing the cross sections. However, the lower partial waves, which are the major contributors to the total cross sections, are governed by the combined action of the $3s \rightarrow 3p \rightarrow 4s$ indirect coupling, distortion, and indirect coupling through other intermediate states. One would, therefore, not expect the second Born approximation to be adequate for the lower partial-wave cross sections. Moreover, it is known that the first Born approximation gives a gross overestimation of the $3\,^2P$ cross section because of the very strong coupling between $3s$ and $3p$. In view of the fact that the $3p \rightarrow 4s$ coupling is also a very strong one, the second Born approximation is likely to overestimate the contribution of the $3s \rightarrow 3p \rightarrow 4s$ indirect coupling to the cross sections since the second Born amplitude due to this indirect coupling route is a suitably weighted convolution of the $3s$-$3p$ and $3p$-$4s$ first Born amplitudes.

IV. EXAMINATION OF APPROXIMATIONS EMPLOYED IN CLOSE-COUPLING CALCULATIONS

The calculations presented in Sec. III were based on the close-coupling expansion along with a number of auxiliary approximations as described in Sec. II. These approximations will be examined in some detail in this section.

TABLE III. Partial-wave excitation cross sections of the $4\,^2S$ state of sodium.[a]

	Q_L in units of a_0^2									
	E = 7.364 eV		E = 10.520 eV			E = 16.832 eV		E = 23.144 eV		
L	2-st	7-st	2-st	3-st	7-st	2-st	7-st	2-st	3-st	7-st
0	1.34	0.23	0.75	0.61	0.09	0.34	0.11	0.20	0.10	0.09
1	6.25	2.89	3.10	1.96	1.66	1.25	0.88	0.68	0.50	0.55
2	5.96	6.05	3.87	2.81	3.51	1.86	1.62	1.06	0.83	0.94
3	1.81	1.36	2.08	1.21	1.76	1.55	1.38	1.06	0.83	0.96
4	0.29	0.24	0.70	0.57	0.44	0.90	0.71	0.79	0.60	0.67
5	0.04	0.18	0.17	0.43	0.28	0.14	0.34	0.48	0.38	0.39
6	0.00	0.07	0.04	0.31	0.21	0.16	0.21	0.25	0.25	0.23
7			0.01	0.20	0.12	0.05	0.17	0.11	0.18	0.15
8						0.02	0.13	0.04	0.14	0.12
9								0.02	0.12	0.10
10								0.01	0.09	0.08

[a] 2-st, 3-st, 7-st mean $3s$-$4s$, $3s$-$3p$-$4s$, and $3s$-$3p$-$3d$-$4s$-$4p$-$4d$-$4f$ close coupling, respectively.

The wave functions of the free atom are taken as antisymmetrized products of the Hartree–Fock–Slater one-electron orbitals. One criterion that may be used to assess the reliability of the atomic wave functions is that of line strength. All the dipole-type ($\Delta l_a = \pm 1$) potential elements of $U_{\nu\mu}(r)$ have a long-range r dependence of the form c/r^2, where c is directly proportional to the square root of the line strength between the initial and final state defined by the potential element under consideration. Thus the long-range behavior of the interaction potential elements would be given correctly if the Hartree–Fock–Slater orbitals could provide accurate values of the line strengths. In Table IV we list the line strengths of thirteen transitions calculated from our Hartree–Fock–Slater wave functions and compare them with the values compiled in the National Bureau of Standards publication *Atomic Transition Probabilities*.[24] Our line

TABLE IV. Comparison of the line strengths (in units of a_0^2) of sodium calculated by the Hartree–Fock–Slater (HFS) wave functions and those listed in Ref. 24.

		Values of $S(nl, n'l')$	
nl	$n'l'$	HFS functions	Ref. 24[a]
$3s$	$3p$	37.6	38.1
$3s$	$4p$	0.310	0.311
$3s$	$5p$	0.0411	0.0415
$3s$	$6p$	0.0120	0.0129
$3p$	$4s$	38.5	36.7
$3p$	$3d$	139	135
$3p$	$4d$	11.0	11.9
$4s$	$4p$	209	197
$4s$	$5p$	2.75	2.72
$4s$	$6p$	0.447	0.444
$3d$	$4p$	353	351
$3d$	$4f$	608	610
$4p$	$4d$	438	420

[a] The uncertainties in the line strengths are given in Ref. 24 as less than 3% for the $3s$-$3p$ case and less than 25% for the rest of the cases listed.

strengths agree with those of Ref. 24 to within the uncertainties given therein. As noted in Sec. III A, the difference between our two-state $3s$-$3p$ results and the corresponding results of Barnes, Lane, and Lin is because of the use of different atomic wave functions. The latter authors used hydrogenic wave functions with an effective charge of 2.92 which reproduces the correct $3s$-$3p$ line strength. A detailed analysis shows that the potential primarily responsible for the difference between the results of Barnes *et al.* and our results is the $3p$-$3p$ self-distortion potential. Even with the rather crude hydrogenic wave functions, the cross sections so obtained differ only by 10% from those derived from the Hartree–Fock–Slater orbitals. To get a further quantitative measure of the adequacy of our choice of wave functions, we have replaced the Hartree–Fock–Slater wave functions by the Hartree–Fock functions,[25] and repeated the $3s$-$3p$-$3d$ close-coupling calculations at 10.520 eV. The $3\,^2P$ and $3\,^2D$ cross sections were found to increase by 5.5 and 6.6%, respectively.

In order to estimate the importance of core interactions that were neglected when we approximated Eq. (10) by Eq. (11), we did a three-state $3s$-$3p$-$3d$ close-coupling calculation at 10.5 eV and a two-state $3s$-$3p$ close-coupling calculation at 4.2 eV including core interactions. The core potential of Eq. (10) was generated using the Hartree–Fock–Slater–type core orbitals. These two test calculations show that for $L \geq 4$ the core effects are negligible. The change in the $L \leq 3$ partial-wave cross sections result in a 4% increase in the $3\,^2P$ total cross section at 10.5 eV and a 10% decrease at 4.2 eV. For $3\,^2D$ excitation, the inclusion of the core interactions altered the cross section by less than 1% at 10.5 eV.

In our calculations the exchange effects between the incident and the atomic electrons have been neglected. This approximation can be justified on the grounds that exchange effects are important only for incident energies slightly above the threshold. Nevertheless, an estimate of the influence of the exchange on the excitation cross sections may be obtained by comparing the with-exchange and without-exchange calculations of Karule and Peterkop.[16] Their two-state $3s$-$3p$ calculations in the energy range 2.5–5 eV show that for $L \geq 4$ the partial-wave cross sections are virtually unaffected by exchange and that inclusion of exchange tends to decrease the $L = 0$–3 partial cross sections, on the average, by about 45%. If we assume, for the purpose of estimation, that in general the electron exchange has no effect on the partial-wave cross sections of $L \geq 4$ but may alter those of $L = 0$–3 by as much as 45% even at higher energies, the inclusion of exchange would then change the $3\,^2P$ and $3\,^2D$ cross sections above 10 eV by no more than 10%. On the other hand, according to this criterion, the $4\,^2S$ cross sections may be much more susceptible to exchange, 40% at 10.5 and 30% at 16.8 eV.

The approximation of truncating the close-coupling expansion of Eq. (3) and the question of convergence have been discussed for excitation of each individual state in Sec. III.

V. DISCUSSION AND CONCLUSIONS

By means of close-coupling calculations we have demonstrated the importance of indirect coupling on the excitation cross sections of the $3\,^2D$, $4\,^2D$, and $4\,^2F$ states in the "intermediate" energy range of 7–24 eV. To obtain excitation cross sections for these states, it is not sufficient to consider just the initial and final states, but the coupling through the intermediate states must also be included. Under the framework of the method of close coupling, the total wave function (of the incident particle and target system) is expanded in terms of the ground state (of the target atom), the final state, and as many intermediate states as is practical. In the case of the $3\,^2D$ state, a very good convergence of the close-coupling expansion is achieved by including the seven states corresponding to $n = 3$ and $n = 4$. This seven-state expansion gives adequate (20%) cross sections for the $4\,^2D$ state. For the $4\,^2F$ state some of the states with $n \geq 5$ may possibly affect the indirect coupling to a greater extent, but we have made no systematic investigation of the convergence behavior. The influence of indirect coupling on the $4\,^2S$ state, however, is considerably smaller than that on the ^2D and ^2F. Of some special interest is the fact that the $3s \rightarrow 3p \rightarrow 3d$ indirect coupling route has the effect of substantially decreasing the $3\,^2P$ cross sections from the values obtained by consideration of the $3s$-$3p$ direct coupling alone.

For energies between 10 and 24 eV, the Born approximation and the two-state close-coupling scheme give nearly identical cross sections for the $3\,^2D$, $4\,^2D$, and $4\,^2F$ states, and show reasonable agreement for the $4\,^2P$ states. This tends to support the validity of the plane-wave portion of the Born approximation. The Born approximation fails for $3\,^2P$ in the "intermediate" energy range as explained in Sec. III A. For the $4\,^2S$ state the agreement between the cross sections computed by the Born approximation and by the two-state close-coupling method is rather poor at 10.5 eV but becomes much better at higher energies. At 10.52 eV the major contributions to the 3^2S-4^2S excitation come from the first few partial waves which are quite susceptible to distortion effects. With increasing energies, the higher partial waves assume a more important role with the results being diminished distortion effects and restoration of the agreement between the Born approximation and the two-state close-coupling scheme.

The numerical procedure of the close-coupling calculation becomes progressively more time consuming as one adds more atomic states to the basis set of the expansion. It would be very desirable if one could introduce some simplifying approximations to the close-coupling scheme so that the latter could be used directly to handle indirect coupling through the higher states which are otherwise not easily included in the basis sets. Our calculations show that the second Born approximation is not satisfactory in the energy range of our interest. For instance a $3s$-$3p$-$3d$ second Born approximation overestimates the $3\,^2D$ cross section at 10.5 eV by more than a factor of 2. We have tried a few versions of an iteration technique in combination with multistate close-coupling calculations, but the results have not yet been completely successful. Nevertheless in the "intermediate" energy range the method of close coupling in its present form proves to be a useful tool for calculating excitation cross sections of dipole-forbidden states for which indirect coupling with the ground state through the dipole-allowed states may be of comparable importance to the direct coupling.

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