# 25-State Calculation for $e^-$-Na$_2$ Scattering

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We use the Schwinger multichannel method with pseudopotentials to study low energy $e^-$-Na$_2$ scattering. Our cross sections, for impact energies from 0 to 10 eV, include polarization effects and up to 25 open channels related to all electronic states lying below 3.5 eV. Our results predict prominent threshold effects due to a very intense coupling between the $B^1\Pi_u$ state and the elastic channel in an energy region where there is no experimental data. Our total 25-state cross sections are in very good agreement with available experimental data for energies below about 4 eV. [S0031-9007(98)07561-9]

Calculations of $e^-$-molecule collision cross sections are useful in supplementing experimental data. If the calculations are from first principles (usually those which keep the many-body character of the problem), the results are especially reliable and can be used as a guide for future experiments. Among the first-principle methods, the Schwinger multichannel method (SMC) [1] has received special attention [2]. Its combination with norm-conserving pseudopotentials (SMCPP) [3] was shown to be useful for molecules made up of heavy atoms [4]. In this Letter we show cross sections for electron-Na$_2$ scattering obtained with the SMCPP for electron impact energies up to 10 eV. The present study represents the most advanced application of our procedures since, in this case, the pseudopotential replaces the majority of the electrons (20 out of 22) and we include the description of many-body features such as electronic excitations and polarization effects simultaneously. Besides, our results show an uncommon strong coupling (to be confirmed experimentally) between the first $B^1\Pi_u$ state and the ground state $X^1\Sigma_g$, and our total cross section is in very good agreement with experimental data at low energies.

The dimer has two valence electrons, being in this respect analogous to H$_2$. Thus, from the point of view of pseudopotentials, that is, after eliminating the core electrons, the two molecules are similar. However, unlike H$_2$, the dimer is a big molecule with a much larger cross section. It also has a very rich spectrum of low-lying excited states and can be considered a low electronic density system for which correlation is important. (The kinetic energy increases as $n^{5/3}$, exchange as $n^{4/3}$, and correlation as $n$, where $n$ is the electronic density. If $n$ is small, the correlation energy is relatively more important.) To reduce the comparison to numbers, the internuclear separations are $3.08 \times 10^{-8}$ cm for Na$_2$ and $0.74 \times 10^{-8}$ cm for H$_2$. Typical total electron scattering cross sections (elastic plus inelastic), in the 1.0 to 10 eV energy range, are of the order of $10^{-14}$ cm$^2$ for Na$_2$ and $10^{-15}$ cm$^2$ for H$_2$. The first excitation threshold for Na$_2$ is 0.73 eV [5], whereas for H$_2$ it is 10.62 eV [6]. Besides, the sodium molecule has an experimental electron affinity

of $A_{\exp} = 0.43$ eV [7]. Thus, the cross sections for H$_2$ [8] are a poor guide to understanding Na$_2$. The dimer is expected to yield much larger cross sections, to be highly polarizable and very easily excitable due to its many low energy excited states.

In the SMC [1], the scattering amplitude is obtained in the molecular body frame for a transition of an electron with wave vector $\vec{k}_i$ and the target in the state $|\Phi_i\rangle$ to a channel where the electron has wave vector $\vec{k}_f$ and the target is left at $|\Phi_f\rangle$. The scattering amplitude is given by

$$f_{\vec{k}_f,\vec{k}_i} = -\frac{1}{2\pi} \sum_{m,n} \langle S_{\vec{k}_f}|V|\chi_m\rangle (A^{(+)^{-1}})_{mn} \langle \chi_n|V|S_{\vec{k}_i}\rangle. \quad (1)$$

Here $|S_{\vec{k}_i}\rangle$ is the input channel state represented by the product of a plane wave with wave vector $\vec{k}_i$ times $|\Phi_i\rangle$, the initial target state (Slater determinant of molecular orbitals). $|S_{\vec{k}_f}\rangle$ has an analogous definition. $V$ is the interaction between the incident electron with the pseudopotentials and with the valence electrons. Exchange and correlation with the core electrons, which are important for the dimer [9], are built into the pseudopotential [10]. The states $|\chi_n\rangle$ form an ideally complete set of $(N+1)$-electron trial functions. $N$ is the number of electrons in the target (two for Na$_2$ treated by pseudopotentials). $A^{(+)^{-1}}$ is the inverse of the matrix $A^{(+)}$ defined as

$$A_{mn}^{(+)} = \langle \chi_m|\frac{(VP + PV)}{2} - VPG_0^{(+)}PV + \frac{1}{N+1}$$
$$\times \left[\hat{H} - \frac{N+1}{2}(\hat{H}P + P\hat{H})\right]|\chi_n\rangle, \quad (2)$$

where $G_0^{(+)} = \frac{\hbar^2}{2m}(E - H_0 + i\epsilon)^{-1}$, $H_0$ is the Hamiltonian for the $N$ electrons of the target plus the kinetic energy of the incident electron, and $E$ is the total energy of the system target + electron. $P$ is a $N$-electron projector onto the open channels. It commutes with $H_0$. Finally $\hat{H} = E - H$, $H$ being the total Hamiltonian for $N+1$ electrons. Because of computational limitations, the number of functions $|\chi_n\rangle$, as well as the sum over the open

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channels in $P$, are truncated. Thus, the quality of the results obtained in a SMC calculation depends on the choice of the terms retained in Eqs. (1) and (2).

Our calculations are carried out in the fixed-nuclei approximation. For all electronic transitions, the Frank-Condon factors are made equal to 1 and for each electronic transition the vibrational states are considered as open. The final cross section is averaged over all molecular orientations. Therefore, in this application, vibrational and rotational channels are not resolved. We use a basis of 68 Cartesian-Gaussian functions ($7s5p2d$ centered on each Na atom) designed for our pseudopotential calculations [11]. The Gaussian function exponents were chosen so that the eigenvalues of the one-electron states $3s$, $4s$, $5s$, $3p$, $4p$, and $3d$ of the Na atom coincided with those obtained numerically with a precision better than 0.001 hartree. The exponents of the $s$ functions are 0.896 131 707 7, 0.337 792 240 2, 0.146 544 494 3, 0.051 303 460 2, 0.011 415 213 0, 0.003 303 821 1, 0.000 781 789 6; of the $p$ functions are 0.928 289 475 8, 0.103 559 405 2, 0.035 603 250 6, 0.012 344 316 0, 0.005 915 813 0; and of the $d$ functions are 0.065 838 782 4, 0.017 092 433 8. These functions are combined into molecular orbitals with which the Slater determinants describing the molecular target are made. The one-particle wave functions are those of the Hartree-Fock solution for the ground state. For the excited states we used "improved virtual orbitals" (IVO) [12]. This set of orbitals is used to construct the projector $P$ over the open channel subspace and the configuration vectors $|\chi_n\rangle$. The SMC is a $\mathcal{L}^2$ method and allows a full expansion of the scattering function in square integrable functions [1]. In our approximation, the ionization potential is 4.7 eV (the experimental value is 4.9 eV [13]). As all 25 open states we study lie below 3.5 eV, the present calculation will test the influence of the continuum states of the target on the cross sections for this energy region. To our knowledge, this calculation describes one of the largest multichannel coupling for electron scattering by molecules in the literature (see, for example, results obtained by Branchett and Tennyson [14] for $H_2$, using full correlated target states, by Winstead and McKoy [15] for CO and by McCurdy et al. [16] for $CH_4$, using in both cases Hartree-Fock targets with IVO's as in the present calculation).

We assume that the incident electron has spin up $\uparrow$. Thus letting $b^\dagger$ and $b$ be creation and annihilation operators of one electron, $|0\rangle$ the vacuum, and $|\Phi_{1\sigma_g}^{(0,0)}\rangle \equiv b_{1\sigma_g\uparrow}^\dagger b_{1\sigma_g\downarrow}^\dagger |0\rangle$ the Slater determinant for the ground state ($1\sigma_g$ is the only occupied one-particle state in the valence of $Na_2$), we consider the first eight triplet excited states of $Na_2$ and their corresponding singlet states. The possible final states of the target can then be written as

$$|\Phi_f^{(S,M_s)}\rangle = \begin{cases} |\Phi_{1\sigma_g}^{(0,0)}\rangle \\ |\Phi_\mu^{(1,1)}\rangle \equiv b_{\mu\uparrow}^\dagger b_{1\sigma_g\uparrow}^\dagger |0\rangle = -b_{\mu\uparrow}^\dagger b_{1\sigma_g\downarrow} |\Phi_{1\sigma_g}^{(0,0)}\rangle \\ |\Phi_\mu^{(1,0)}\rangle \equiv \frac{1}{\sqrt{2}} (b_{\mu\uparrow}^\dagger b_{1\sigma_g\downarrow}^\dagger + b_{\mu\downarrow}^\dagger b_{1\sigma_g\uparrow}^\dagger)|0\rangle = \frac{1}{\sqrt{2}}(b_{\mu\uparrow}^\dagger b_{1\sigma_g\uparrow} - b_{\mu\downarrow}^\dagger b_{1\sigma_g\downarrow})|\Phi_{1\sigma_g}^{(0,0)}\rangle \\ |\Phi_\mu^{(0,0)}\rangle \equiv \frac{1}{\sqrt{2}} (b_{\mu\uparrow}^\dagger b_{1\sigma_g\downarrow}^\dagger - b_{\mu\downarrow}^\dagger b_{1\sigma_g\uparrow}^\dagger)|0\rangle = \frac{1}{\sqrt{2}}(b_{\mu\uparrow}^\dagger b_{1\sigma_g\uparrow} + b_{\mu\downarrow}^\dagger b_{1\sigma_g\downarrow})|\Phi_{1\sigma_g}^{(0,0)}\rangle. \\ \text{for } \mu = 1\sigma_u, 2\sigma_u, 2\sigma_g, 3\sigma_g, 1\pi_u^\pm, 2\pi_u^\pm, 1\pi_g^\pm, 1\delta_g, \end{cases}$$

where the superscript $S = 1$ or 0 indicates a triplet or singlet state, respectively, and $M_s = 0$ or 1 refers to the spin $z$ component of this state.

The operator $P$ is a sum over the final states $|\Phi_f^{(S,M_s)}\rangle$ (open channels). The number of terms in $P$ depends on the impact energy and increases as this energy reaches each excitation threshold of Table I. A general expression for $P$ is

$$P = \sum_{\mu,(S,M_s)}^{\text{open}} |\Phi_\mu^{(S,M_s)}\rangle\langle\Phi_\mu^{(S,M_s)}| + |\Phi_{1\sigma_g}^{(0,0)}\rangle\langle\Phi_{1\sigma_g}^{(0,0)}|. \quad (4)$$

The configuration vectors $|\chi_n\rangle$ are the possible final states to which is added the $(N + 1)$th electron,

$$|\chi_n\rangle = \begin{cases} b_{\nu\uparrow}^\dagger |\Phi_{1\sigma_g}^{(0,0)}\rangle \\ b_{\nu\uparrow}^\dagger |\Phi_\mu^{(1,0)}\rangle \\ b_{\nu\downarrow}^\dagger |\Phi_\mu^{(1,1)}\rangle \\ b_{\nu\uparrow}^\dagger |\Phi_\mu^{(0,0)}\rangle, \end{cases} \quad (5)$$

where $n$ is a composite index representing the target state and the one-particle scattering functions $\nu$. The $\nu$ are all the solutions of the Hartree-Fock equations [12], except the one for the occupied orbital in the ground state.

As a preliminary test for our scattering calculations, we calculated the electron affinity of the $Na_2$ molecule in two different situations: the first one was calculated considering only the vectors of the type $b_{\nu\uparrow}^\dagger|\Phi_{1\sigma_g}^{(0,0)}\rangle$ in the calculation of the lowest eigenvalue of the $(N + 1)$-particle Hamiltonian $H$. This configuration space is characteristic of a static-exchange scattering calculation and the resulting electron affinity is $A_{\text{se}} = 0.04$ eV. The electron affinity calculated with the complete configuration space [Eq. (5)], used to describe the polarization of the molecular target, is $A_{\text{pol}} = 0.46$ eV, which is very close to the experimental value. The difference between $A_{\text{se}}$ and $A_{\text{pol}}$ indicates that polarization effects are very important in the study of electron scattering by $Na_2$.

We first studied the total cross sections (elastic plus inelastic) including only the $B^1\Pi_u$ excited state. At the

TABLE I.  Calculated excitation thresholds for $Na_2$.

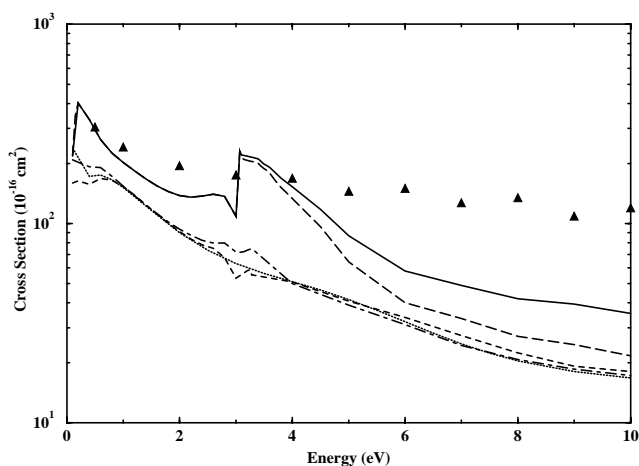| State | Energy (eV) |
|---|---|
| $1^3\Sigma_u$ | 0.441 |
| $1^3\Pi_u$ | 1.099 |
| $1^3\Sigma_g$ | 1.746 |
| $1^1\Sigma_u$ | 2.477 |
| $1^3\Pi_g$ | 2.840 |
| $2^3\Sigma_g$ | 2.981 |
| $B^1\Pi_u$ | 3.064 |
| $2^3\Sigma_u$ | 3.272 |
| $2^1\Sigma_g$ | 3.273 |
| $1^1\Pi_g$ | 3.326 |
| $2^3\Pi_u$ | 3.333 |
| $1^3\Delta_g$ | 3.367 |
| $2^1\Sigma_u$ | 3.437 |
| $3^1\Sigma_g$ | 3.459 |
| $2^1\Pi_u$ | 3.516 |
| $1^1\Delta_g$ | 3.587 |



FIG. 1.  Total (elastic plus inelastic) cross sections. Solid line: total cross section in the $X^1\Sigma_g + B^1\Pi_u$ calculation; dashed line: elastic cross section in the $X^1\Sigma_g + B^1\Pi_u$ calculation; dot-dashed line: total cross section in the $X^1\Sigma_g + 2^3\Sigma_g$ calculation; short-dashed line: total cross section in the $X^1\Sigma_g + 2^3\Sigma_u$ calculation; dotted line: static-exchange calculation. Triangles: Experimental total cross section [18].

impact energy of 0 eV the projector $P$ has only one term defined by the ground state of the molecule (elastic calculation). As the impact energy reaches the $B^1\Pi_u$ excitation threshold (see Table I), this channel is opened and $P$ is increased by two terms, since it is a twofold degenerate state. In Fig. 1, the solid and the long-dashed lines show the 3-state calculations for total and elastic cross sections, respectively, including the ground state and the $B^1\Pi_u$ excited state. The dotted line shows the static-exchange results. For energies below the excitation threshold these results show that the $B^1\Pi_u$ state is very important in the description of polarization effects, since its presence as a closed channel increases the values of the cross sections by more than 30% compared to the static-exchange result. Figure 1 also shows 2-state total cross sections for $(X^1\Sigma_g + 2^3\Sigma_g)$ and $(X^1\Sigma_g + 2^3\Sigma_u)$ calculations. The $2^3\Sigma_g$ and $2^3\Sigma_u$ are the first excited states of $Na_2$ below and above the $B^1\Pi_u$, respectively. The two curves are smooth (except for small variations around the thresholds) and close to the static-exchange results, which indicates that these states give a small contribution to polarization effects. Another interesting feature of the $B^1\Pi_u$ 3-state total cross sections is a structure that appears at the excitation threshold. We see in Fig. 1 that the origin of this discontinuity is related to a strong coupling between the $B^1\Pi_u$ and the elastic channels. This coupling is so strong that the elastic cross section jumps from $109 \times 10^{-16}$ to $229 \times 10^{-16}$ cm² at the threshold. Unfortunately, there is a lack of experimental points in this energy region. Calculations with a different basis set including 80 basis functions reproduce all these features of the 3-state $(X^1\Sigma_g + B^1\Pi_u)$ total cross sections. This behavior of the $B^1\Pi_u$ 3-state cross sections of the $Na_2$ molecule seems to be a consequence of the exceptionally strong transition probability of the $3s \rightarrow 3p$ excitation of the

sodium atom [17] (this may be understood through the calculation of the molecular orbitals $1\sigma_g$ and $1\pi_u^{\pm}$ by noting that the $3s$ and $3p$ atomic orbitals represent their largest components). Next, in Fig. 2 we show our results considering up to 25 open channels. All these states are included in the configuration space [Eq. (5)], which is composed of 2257 functions with overall symmetries running from $^2\Sigma_{g,u}$ up to $^2\Phi_{g,u}^{\pm}$. For impact energies above 3.587 eV, all the 25 studied channels are open, so that, for higher energies, the molecular distortion is made through multichannel coupling. We compare these results to our static-exchange calculation and to experimental total cross sections [18]. The inclusion of the other excited states of the molecule corrects the 3-state $(X^1\Sigma_g + B^1\Pi_u)$ total cross section and the final result is very close to the experimental data for low energies (the continuum states of the target seem to be of no importance in this energy region). The vertical line at 3.521 eV indicates that, up to this energy, all possible excited states (23 states—see Table I) are included as open channels (3.521 eV is the excitation threshold for the $3^3\Sigma_g$ state, not included in this calculation). For impact energies above about 4 eV the experimental data take larger values than ours. This indicates that there are excited states of the molecule which are important in this energy region and are not included in our calculation. Besides, the continuum states of the target play an important role for impact energies above the ionization threshold [19] and are not considered here. The strong coupling between the $B^1\Pi_u$ and the elastic channel is not affected by the inclusion of the other excited states of the molecule and is still present on the total cross section, as a fingerprint of the $Na_2$ $B^1\Pi_u$ excited state.
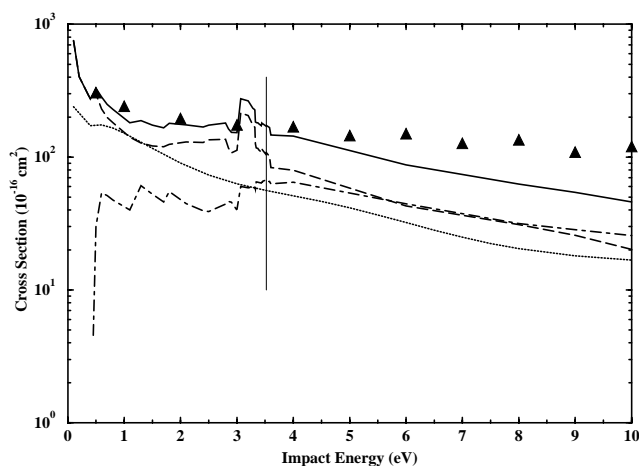
FIG. 2. 25-state calculation for $Na_2$. Solid line: total (elastic plus inelastic) cross section. Dashed line: elastic cross section. Dot-dashed line: excitation (inelastic) cross section. Dotted line: cross section in the static-exchange approximation. Triangles: Experimental total cross section [18]. The vertical line (at 3.521 eV) indicates that, up to this energy, all possible excited states are included as open channels in all calculations, except in the static-exchange result (dotted line).

The $Na_2$ molecule presents a very large excitation cross section, even larger than the elastic one (in this level of approximation) for impact energies above 8 eV. The excitation cross section, represented by the dot-dashed line of Fig. 2, shows many structures, each one associated to the opening of one of the studied channels.

The good agreement with experiment indicates that *ab initio* methods like the SMCPP are powerful frameworks to study complicated problems as the electron-$Na_2$ scattering and may produce reliable results when the important phenomena are considered. The ability of the method to treat the many-body character of the problem allows us to study details of the cross sections as threshold behaviors. Other theoretical results calculated with other methods in similar approximations and measurements of total cross sections for a larger number of impact energies are desirable for a complete understanding of the problem.

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