Effective configurations in electron-molecule scattering. II

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We present results of the application of the Schwinger multichannel method using effective configurations [Azevedo *et al.*, Phys. Rev. A **61**, 042702 (2000)] to study special features of low-energy electron-molecule scattering, such as (i) the shape resonance in e^--N_2 scattering; (ii) the Ramsauer-Townsend minimum in e^--CH_4 scattering; and (iii) a Feshbach resonance in e^--H_2 scattering (in a two-channel coupling calculation including polarization effects). In all cases, we find that the use of effective configurations to describe polarization effects allows a substantial reduction of the configuration space, without any loss of quality of the results. The present applications (together with our previous study of nonresonant electron-H_2 scattering) indicate that this technique will be very useful in the analysis of more complex systems.

Polarization effects are very important during low-energy electron-molecule collision processes. Electrons with less than about 7 eV of energy are sufficiently slow to experience an electronic cloud deformation during the collision time. As a consequence, the interaction potential is substantially modified when compared to the so-called static-exchange potential. As a result, the theoretical predictions may change dramatically. For example, existing shape resonances may be moved to lower energies, Ramsauer-Townsend minima, which usually are not present in the static-exchange approximation, may appear for some molecular targets, and core-excited shape resonances may become Feshbach resonances when polarization effects are taken into account.

If a resonance is associated with the target ground state and is caused by a finite penetrable potential barrier formed by the combination of centrifugal, static, exchange, and polarization potentials, it is known as shape resonance [1]. It happens, for instance, in the overall $^2\Pi_g$ symmetry in e^--N_2 elastic scattering at around 2 eV of impact energy. On the other hand, a resonance may also be associated with an electronically excited state with the main component (considering that the wave function of $N+1$ electrons is expanded as a combination of Slater determinants, where N is the number of electrons in the target state) consisting of a hole in an occupied orbital and two electrons in unoccupied orbital(s) (corresponding to the scattered and excited electrons). These are called core-excited resonances, which may be further classified as (i) Feshbach resonances, where the $N+1$ electron compound state lies below its "parent," N particles, excited state; and (ii) core-excited shape resonances, where the $N+1$ electron compound state lies above its "parent," N-electron state [1]. An example of a Feshbach resonance occurs in e^--H_2 scattering (where the $a\,^3\Sigma_g^+$ state is the main parent) and it may decay either to the elastic ($X\,^1\Sigma_g^+$) channel or to the first electronic excited state ($b\,^3\Sigma_u^+$) channel.

Another interesting feature in electron-molecule (or atom) scattering is the Ramsauer-Townsend minimum. In this case,

a special combination of attractive and repulsive potentials may cause the lowest angular momentum component of the phase shift to vanish, causing a minimum in the cross section (sometimes the same effect is caused by a very attractive potential, making the lowest phase shift go through π). In all these cases, polarization effects play a very important role. As a consequence, a theory will be predictive only if it includes these effects in a proper manner. In this paper, we present results of applications of the Schwinger multichannel method (SMC) using effective configurations [2] to study these special features of low-energy electron-molecule scattering. In particular, we analyze (i) the shape resonance in e^--N_2 scattering; (ii) the Ramsauer-Townsend minimum in e^--CH_4 scattering; and (iii) the Feshbach resonance in e^--H_2 scattering described above. We first present a brief summary of the SMC method and how the effective configurations are generated and used in this formalism. Then, we show the results for each one of the applications, and finish the paper with the conclusions.

The SMC method has been described in detail previously [3] and we only review here the important steps for a complete understanding of our approximations. The method is a multichannel version of the Schwinger variational principle. The trial wave function is expanded in a basis set of square integrable functions (L^2 space) which facilitates the calculation of integrals. The scattering amplitude in the body frame is

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

where

$$d_{mn}=\langle\chi_m|A^{(+)}|\chi_n\rangle \quad (2)$$

and

$$A^{(+)}=\frac{1}{2}(PV+VP)-VG_P^{(+)}V+\frac{1}{N+1}\left(\hat{H}-\frac{N+1}{2}\right.$$
$$\left.\times(\hat{H}P+P\hat{H})\right), \quad (3)$$

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where $G_P^{(+)}$ is the free-particle Green's function projected onto the assumed open channel space through the projection operator P. In the SMC method, P defines the channel-coupling level of the problem and it is constructed with target eigenfunctions, Φ_n. In the present work, the projector P has only one term in the case of e^--N_2 scattering, as well as in the case of e^--CH_4 scattering (elastic processes), i.e., in both these cases, P is the projector onto the ground states of the molecules. In the e^--H_2 scattering case, P has two terms, one corresponding to the ground state $X\,^1\Sigma_g^+$ and the other to the first excited state $b\,^3\Sigma_u^+$. In the above expressions, χ_n are Slater determinants of $(N+1)$ particles used in the expansion of the trial wave function, V is the exact interaction potential between the incident electron and the target, and $\hat{H}$ is the total collision energy minus the full Hamiltonian of the system. The simplest case is the static-exchange level of approximation for an elastic scattering, where χ_n are constructed by adding one-particle (described as combinations of virtual orbital $|\phi_m\rangle$) states to a frozen representation of the ground state of the molecule $|\Phi_0\rangle$, i.e.,

$$|\chi_m\rangle = \hat{A}|\Phi_0\rangle|\phi_m\rangle, \qquad (4)$$

where $\hat{A}$ is the antisymmetrization operator. Inclusion of polarization effects is accomplished by enlarging the space of $N+1$ basis functions (χ_n) through the inclusion of states composed of one-particle orbitals coupled to single-particle excitations of the target, i.e., functions of the type

$$|\chi_m\rangle = \hat{A}|\Phi_i\rangle|\phi_s\rangle, \qquad (5)$$

where the index m stands for both indices i and s, and i runs over singly excited states of the target and s over the virtual orbital set. An n-channel-coupling approximation, with the inclusion of polarization effects, is obtained by using n target states in the expansion of the P projector, and also, at the same time, by letting the number of target states that defines the $|\phi_m\rangle$ space be greater than n.

In our previous work [2], we have proposed a way of reducing the number of configurations (and, as a consequence, the size of all matrices whose dimensions depend on this number) necessary to describe appropriately polarization effects in electron-molecule scattering within the SMC method. As a first step, the full Hamiltonian for the system molecule plus incoming electron (the H_{N+1} Hamiltonian) is diagonalized within a conveniently chosen set of Slater determinants of $N+1$ electrons, which will be called $|\chi_m\rangle_{\text{full}}$. The effective configurations (EC's) will be selected from the space spanned by the H_{N+1} Hamiltonian eigenstates. To do so, an energy cutoff E_{cut} is defined in such a way that all eigenstates with eigenvalues E_{EC} such that $E_{\text{EC}} - E_0 \leqslant E_{\text{cut}}$, where E_0 is the lowest-energy eigenvalue, *may* be used to expand the scattering wave function. Let us call this set EC_1. From this set of configurations, we select a subset, EC_2, that will comprise the final EC's that are actually going to be used in the expansion of the scattering wave function. To make this final selection, we use the diagonal elements of the $(PV+VP)$ matrix calculated using the eigenstates from the

EC_1 set. Another cutoff, $(PV+VP)_{\text{cut}}$, is chosen such that only the EC's that have an absolute value of the diagonal element larger than $(PV+VP)_{\text{cut}}$ will be included in the EC_2 set. The diagonal element of $(PV+VP)$ is the average value of this operator for a particular EC. As each EC is, in principle, a linear combination of open- and closed-channel types of configurations, as defined in Eqs. (4) and (5), the diagonal element of $(PV+VP)$ takes into account the coupling between open-open and open-closed channels and, therefore, it is related to the range of the scattering potential. A trial wave function will only contribute to the scattering if both the wave function and the scattering potential V are nonzero in the same region of space. This is at the heart of the SMC method (and of the regular Schwinger variational method [4]). We now apply this technique to the three scattering problems mentioned before, viz., e^--N_2, e^--CH_4, and finally the e^--H_2 scattering.

The e^--N_2 scattering process has been studied in great detail by many groups, and we only cite here some of the most recent experimental and theoretical work [10,26–28]. For further details, the reader should consult the references listed in these papers. The shape resonance in the e^--N_2 scattering is, probably, the most studied shape resonance in the literature. As resonances are quasibound states, we expect the effective configurations, which are eigenstates of the full Hamiltonian within the $|\chi_m\rangle_{\text{full}}$ space, to describe them well. We performed a calculation considering nitrogen at the experimental geometry $R_0 = 2.068a_0$ [5]. The Cartesian Gaussian basis set that we have used (centered on each nitrogen atom) was obtained in the following way: the coefficients and exponents for the contracted $1s$ functions were extracted from Table 7.87.1 of Ref. [6] [core($1s$) exponents 5909.440, 887.4510, 204.7490, 59.837 60, 19.998 10, 7.192 740, 2.685 980; and core($1s$) coefficients 0.001 190, 0.009 099, 0.044 145, 0.156 404, 0.356 741, 0.446 533, 0.145 603]. The exponents for the other Cartesian Gaussian basis functions were obtained via a variational technique [7] (type s: 7.496 286 0, 0.725 866 0, 0.227 837 0; type p: 7.795 695, 0.846 434, 0.307 125, 0.105 919; and type d: 0.941 374, 0.245 400, 0.077 519). With this basis we obtain a SCF energy of -108.947 a.u. and the values of 15.03 and 9.87 (in atomic units) for the parallel and perpendicular components of the polarizability, respectively. These results are in good agreement with experimental data [8,9].

In Fig. 1, we show results for e^--N_2 elastic scattering for the $^2\Pi_g$ symmetry considering static-exchange plus polarization effects obtained with the full reference calculation ($|\chi_m\rangle_{\text{full}}$ space). It was done considering holes in the σ_g, π_{ux}, and π_{uy} orbitals, and all single virtual excitation that the basis sustains, which results in a total of 2696 configurations. At this level of approximation the resonance position is at 1.6 eV, and appears on the left side of the experimental position [2.39 eV] [10]. This is due to overcorrelation [11] (it means imbalance between the target and anion N_2^- state descriptions). Recently, Winstead and McKoy [12] proposed a more compact way to select configurations in scattering resonant channels. Using their criterion, we reduce the number of configurations to 728, and the resonance position
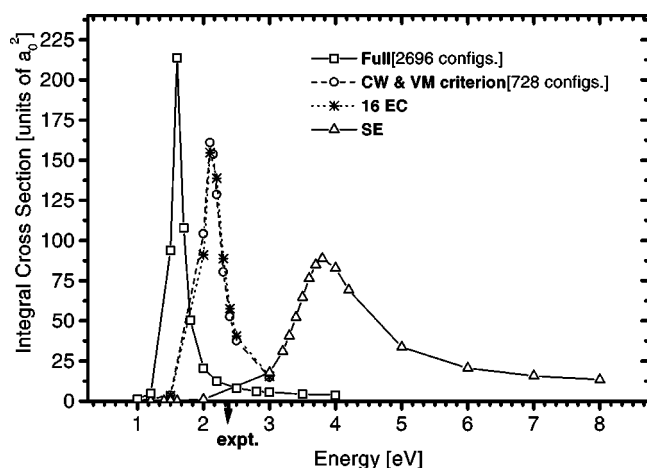
FIG. 1. $^2\Pi_g$ integral cross section for e^--N_2 elastic scattering. Full means the reference calculation considering holes in the σ_g, π_{ux}, and π_{uy} orbitals and all single virtual excitation that the basis sustains, resulting in a total of 2696 configurations. CW and VM is the same approximation but now making use of the Winstead and McKoy criterion [12]. We reproduce these last results with 16 effective configurations (EC's) using an E_{cut} of 20 eV and a $PV + VP_{cut}$ of 1.0×10^{-4}. For completeness, we also present the static-exchange approximation (SE).

FIG. 2. A_1 symmetry integral cross section for e^--CH_4 elastic scattering. Full means the reference calculation considering holes in the four highest occupied orbitals and all single virtual excitations that the basis sustains, which results in a total of 5850 configurations [17]. CW McCurdy are the results extracted from Ref. [14]. Our results using effective configurations were obtained with an E_{cut} of 20 eV and a $PV + VP_{cut}$ of 1.0×10^{-4}, which gave a total of 80 EC's and with an E_{cut} of 50 eV and a $PV + VP_{cut}$ of 1.0×10^{-4}, which resulted in a total number of 601 EC's.

moves to 2.1 eV. At last, we apply the effective configuration technique to this 728-configurations space, with E_{cut} equal to 20 eV and a $PV + VP_{cut}$ equal to 1.0×10^{-4}. With these cutoffs, we obtain only 16 EC's, and the results show that they are enough to reproduce not only the form but also the position of the resonance. We have added to the figure the results for the static-exchange approximation, in order to show that inclusion of polarization effects changes dramatically the cross section at low scattering energies, and therefore they cannot be neglected.

The e^--CH_4 scattering process is the most studied among the polyatomic systems. One of the reasons is the presence of a valley in the integral cross section at about 0.4 eV, known as a Ramsauer-Townsend minimum. This feature is due to a special combination of the potentials involved (static, exchange, and polarization potentials). There is a very large number of theoretical works on the Ramsauer-Townsend minimum in the e^--CH_4 scattering system [13–16]. As the minimum is not a resonant feature, it represents a good test for our procedure. Recently, we have presented a calculation [17] for CH_4 using the SMC method with BHS pseudopotentials [18]. In this methodology, we have replaced the inner-core electrons by a soft pseudopotential, as implemented by Bettega et al. [19] in our SMC electron-molecule computer codes. We took the C—H bond length as 2.05 a.u. In order to have a better description of the scattering wave function, we have also included additional centers placed at 0.75 a.u. from the carbon atom. The exponents of the uncontracted Cartesian Gaussian basis functions used were 2.648 201, 0.578 047, 0.176 324, 0.034 012, 0.013 014 for s functions; 3.823 468, 0.835 457, 0.193 432, 0.042 745 for p functions; and 0.102 265 for a d function. The four additional centers contained p functions with an exponent equal to 0.65. With this basis set, we have made all possible single virtual
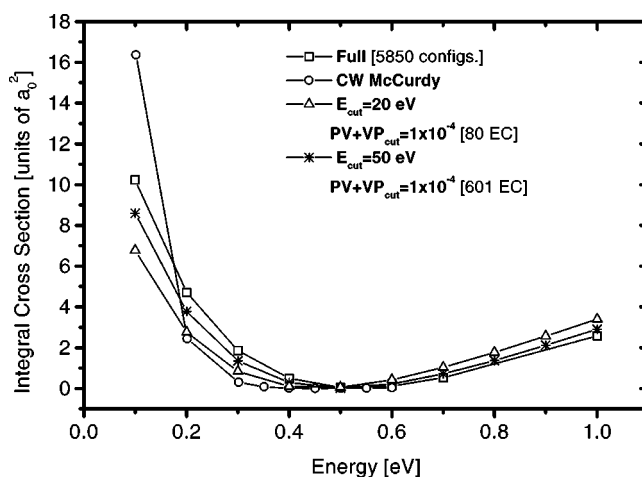
excitations out of the highest four occupied orbitals of the molecule. Within this approximation, we obtained a total number of 5850 scattering configurations for the $A1$ symmetry (C_{2v} point group) [17]. This is our present reference (full) calculation. In Fig. 2, we show the integral cross section for the $A1$ symmetry (only the angular momentum $l = 0$ component). With an E_{cut} equal to 20 eV and a $PV + VP_{cut}$ equal to 1.0×10^{-4}, we obtain a set of 80 configurations, which already shows a good agreement with the full reference calculation. The effective configuration space contains only 1.4% of all possible configurations. To check convergence, we also show the results obtained with E_{cut} equal to 50 eV (10% of all the configurations).

We now turn to a more sophisticated physical process, the so-called Feshbach resonance. This kind of resonance can only be treated within a many-body theory framework. One of the first theoretical results for H_2 was obtained by da Silva et al. [20]. More recently, Tennyson's group have published a very complete set of papers on this subject [21,22]. Over the past 30 years, many experiments have been performed on the e^--H_2 scattering, as well as several theoretical studies. Just as a guide, we only cite the most recent experimental [23] paper, as well as the most recent multichannel theoretical studies [24,25], and suggest their references for further reading.

In the present application we have used nine s functions (exponents 39.186 359, 6.567 806 2, 1.774 537 5, 0.623 416 8, 0.235 659, 0.089 189 0, 0.036 337 810, 0.015 303 560, 0.005 615 930 0) and four p functions (exponents 5.6, 1.4, 0.178 571, 0.05) centered on the H atoms, plus two additional d functions (exponents 0.041 835, 0.011 785) centered in the middle of the H—H bond. With this basis we obtained an SCF energy of -1.133 a.u. at the equilibrium
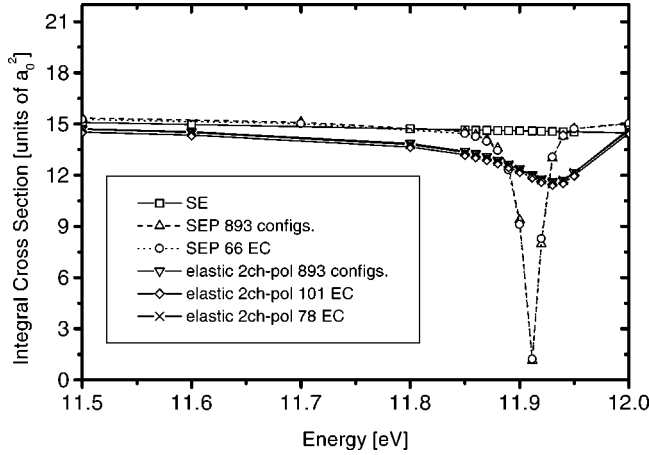
FIG. 3. $^2\Sigma_g^+$ integral cross section for e^--H$_2$ elastic scattering at the static-exchange approximation (SE), static-exchange plus full polarization set (SEP), and using effective configurations with E_{cut} = 20 eV and $PV+VP_{cut}$ = 1.0×10^{-5}, which resulted in 66 EC's. We also show the elastic part of a two-channel plus polarization (elastic 2chn-pol) calculation when all the 893 configurations are included and when an energy criterion of E_{cut} = 20 eV was used with $PV+VP_{cut}$ = 1.0×10^{-4} (78 EC's) and with $PV+VP_{cut}$ = 1.0×10^{-5} (101 EC's).

internuclear distance of $1.4a_0$. The vertical energy excitation for the $b\,^3\Sigma_u^+$ state (described with an improved virtual orbital) was 9.966 eV, which is in good agreement with the ''experimental'' vertical excitation energy of 10.35 eV. With this basis set, we can generate a total of 893 configurations that can be used in the expansion of the scattering wave function. This defines the full $|\chi_m\rangle_{full}$ space of configurations. Figure 3 shows the results of the elastic scattering cross section using the static exchange, the static exchange plus full polarization, and static exchange plus polarization using the effective configurations all for the $^2\Sigma_g^+$ symmetry. We observe that the inclusion of polarization effects in this case changes substantially the cross sections (a narrow deep is seen in the one-channel level of approximation, whereas a broad deep is seen in the two-channel level of approximation). The observed structure in the cross section is the manifestation of a core-excited Feshbach resonance. The compound state has an energy level whose main component is associated to the $a\,^3\Sigma_g^+$ parent state, which lies just above it. The broader cross-section curve in the two-channel approximation is a result of the inclusion of the competing channel $b\,^3\Sigma_u^+$ state as an open channel. Our present results obtained with 66 EC's reproduce well the results obtained with the full 893 configurations, as would be used in the conventional Schwinger multichannel method. In Fig. 3, we also present the elastic integral cross section for the two-channel calculation ($X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ states as open channels). As can be seen in this figure, the resonant structure is not very pronounced in the elastic channel, because the Feshbach resonance decays preferentially into the inelastic $b\,^3\Sigma_u^+$ channel. Figure 4 shows the electronic excitation cross section of the
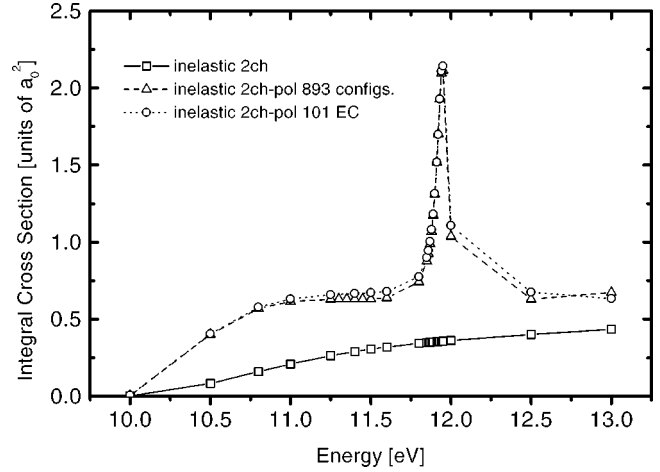

FIG. 4. $^2\Sigma_g^+$ integral cross section for the $X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$ excitation. 2chn means a two-channel approximation including the $X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ states of H$_2$. In the 2ch-pol calculation, we also included polarization effects (all other target states that the basis can sustain as closed channels), which resulted in a total number of 893 configurations. We also show a 2ch-pol calculation performed with effective configurations with E_{cut} = 20 eV and $PV+VP_{cut}$ = 1.0×10^{-5}, which resulted in 101 EC's.

$b\,^3\Sigma_u^+$ state. The observed narrow peak clearly shows the preference of the Feshbach resonance to decay to this state instead of to the ground state. As discussed by da Silva et al. [20], the reason for this is the allowed dipole coupling between the $a\,^3\Sigma_g^+$ and $b\,^3\Sigma_u^+$ states. The number of EC's used in the two-channel approximation (we show results using 78 and 101 EC's) is slightly bigger than the number used in the one-channel approximation (66 EC's) because the presence of the $b\,^3\Sigma_u^+$ state in the projector P increases the range of the potential.

In conclusion, we can say that the use of effective configurations retains all physical properties of three classical phenomena of the scattering process: (i) shape resonances, as observed in e^--N$_2$ scattering; (ii) the Ramsauer-Townsend minimum, as it appears in e^--CH$_4$ elastic scattering; and (iii) in the treatment of a Feshbach resonance at the one- and two-channel level of approximation (with polarization effects) in e^--H$_2$ scattering. The main advantage in using effective configurations is the reduction in the size of all matrices involved in the calculation [especially the $A^{(+)}$ matrix of Eqs. (1) and (2), which needs to be inverted]. Such a reduction will be very useful in the study of more complex systems, where the configuration space will become very big (it increases as the product of the number of hole orbitals times the number of unoccupied particle orbitals times the number of scattering basis functions).

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