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Effective configurations in electron-molecule scattering

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We present a more efficient way of treating polarization effects in the scattering of low-energy electrons by molecules within the Schwinger multichannel (SMC) method. We propose to expand the scattering wave function in a set of functions of $N+1$ electrons that describe the scattering in an effective way, which allows the use of a small number of functions to describe the polarization effects. As a first test, we apply the method to the scattering of electrons by the H_2 molecule. We calculate elastic integral and differential cross sections, and we obtain excellent results with a reduction in the number of configurations of up to 98% when compared to the traditional method used in the SMC method. This is a substantial size reduction of all matrices involved in the SMC method and, as a consequence, it represents a promising technique for treating more complex molecular systems.

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During the scattering of low energy electrons by molecules there is a significant amount of rearrangement of the molecular electron cloud. These electronic rearrangements are broadly named polarization effects, with a clear link to the polarization of the molecule in the presence of an external electric field. How important these rearrangements are depend on the velocity of the incoming electron and the time scale for the relaxation of the molecule's electron cloud. When the incoming electron is fast enough, it is generally a good approximation to neglect this relaxation completely, and simply consider that the electron is scattered by a static, unrelaxed electron cloud. It is also necessary, of course, to take into account the fact that the incoming electron is indistinguishable from the molecule's electrons. This leads to the so called exchange interaction, and a calculation performed at this level of approximation, i.e., neglecting the relaxation effects, is said to be performed at the static-exchange level. However, for low impact energies the polarization effects cannot be neglected. A classic case is the Ramsauer minimum in the cross section for electron scattering by CH_4.

We present in this paper a method to account for polarization contributions to the scattering cross sections within the Schwinger multichannel (SMC) method. The SMC method without [1] and with pseudopotentials [2] has been very successful in the calculations of elastic and inelastic cross sections for the scattering of electrons by molecules. In the SMC method, the scattering wave function is expanded in a set of Slater determinants, or configurations, and it allows calculations either at the static-exchange level only, or with inclusion of polarization effects. However, the configuration space in this latter case usually grows very large, which forbids the proper inclusion of polarization effects for large molecular systems.

The molecular polarizability can be calculated with reasonable accuracy without the inclusion of correlation effects, and taking into account only the relaxation of the orbitals. If we think in terms of a Hartree-Fock (HF) reference state for the target, in the absence of the electric field, the polarizability calculation would involve only single excitations from this reference state, which is enough to describe the orbital relaxation. This makes the calculation of molecular polarizability a relatively simple task. However, *this is not true in the scattering case*. To make this point more clear, let us take the same HF reference state discussed above. Even if we think that the polarization of the target electron cloud could still be described by single excitations, as the scattering wave function requires configurations in a space of $N+1$ electrons, this implies that the N-electron single excitations must be multiplied (and properly antisymmetrized) by an extra scattering orbital. In practice, this means that the number of configurations of $N+1$ electrons that must be used to describe the scattering wave function can grow very large.

One option to remedy this problem would be an arbitrary selection of which configurations should be included in the expansion of the scattering wave function. This could be physically motivated by arguing which excitations should be more important in the scattering process. However, there is always the danger that some relevant configurations are not being included. Moreover, this approach is not systematic enough to be easily applied to different situations. Another option is to choose more appropriate orbitals to build the configurations. Along this line are the polarized orbitals [3], improved virtual orbitals [4], and modified virtual orbitals [5], which were introduced in the same spirit that natural orbitals [6] are introduced in bound state problems to improve the convergence of configuration interaction calculations. Even though this approach may reduce the number of *orbitals* needed to describe the polarization effects, the number of *configurations* is still large, because, as we mentioned before, each N-electron excited state must be multiplied by a scattering orbital. The polarized orbitals were chosen to describe well the relaxation of the target, and were not optimized to be scattering orbitals. Therefore, a large number of scattering orbitals may still be needed, which will in turn lead to a large configurational space. For electron-molecule scattering calculations, the complex Kohn method [7] used polarized orbitals to speed convergence of the configuration space while the SMC method has used natural orbitals [8], and more recently, modified virtual orbitals and polarized orbitals [9] for this same purpose.

As can be seen, an optimal approach would be not a selection of more effective orbitals, but rather a direct selection of effective configurations. This is exactly what we propose in the present paper. As will be described below, we have devised a way of selecting configurations that lead to a rapid convergence of integral, as well as differential, cross sections as a function of the number of configurations. They are, therefore, describing the scattering in an effective way, and we have named them effective configurations (EC's). The EC's allow a substantial size reduction of all matrices involved in the SMC method, which will be very useful for more complex molecular systems. As a first application of the method, we have chosen the elastic scattering by H_2. It was chosen because it is a simple system, extremely well characterized, and allows us to perform not only converged calculations to take as a reference, but also exploratory tests which are necessary when a new method is proposed.

The SMC method [1] has been described in great detail in many previous publications, and we only review here the main equations which are important for our analysis. The scattering wave function is expanded in Slater determinants of $N+1$ electrons as

$$|\Psi^{(\pm)}_{(\vec{k})}\rangle=\sum_{m} a^{(\pm)}_{m}(\vec{k})|\chi_m\rangle, \tag{1}$$

where $a^{(\pm)}_{m}(\vec{k})$ are variational parameters. The set of Slater determinants $|\chi_m\rangle$ defines the configuration space used to expand the scattering wave function. For a static-exchange calculation, where polarization effects are completely neglected, the Slater determinants used are formed from antisymmetrized products of the target ground state wave function, $|\phi_1\rangle$, by one-electron functions $|\varphi_i\rangle$, i.e.,

$$|\chi_m\rangle=A|\phi_1\rangle|\varphi_i\rangle, \tag{2}$$

where A is an antisymmetrizer. To treat polarization effects in the calculation, the space of configurations is enlarged through the inclusion of configurations of the type

$$|\chi_m\rangle=A|\phi_j\rangle|\varphi_k\rangle, \quad j\geqslant 2, \tag{3}$$

where the $|\phi_j\rangle$, $j\geqslant 2$, are virtual states of the molecular target, obtained from its ground state $|\phi_1\rangle$ by single excitations. The $|\varphi_k\rangle$ are one-electron functions, as before. The resulting expression for the scattering amplitude is

$$[f_{\vec{k}_i,\vec{k}_f}]=-\frac{1}{2\pi}\sum_{m,n}\langle S_{\vec{k}_f}|V|\chi_m\rangle(d^{-1})_{mn}\langle\chi_n|V|S_{\vec{k}_i}\rangle, \tag{4}$$

where

$$d_{mn}=\langle\chi_m|A^{(+)}|\chi_n\rangle, \tag{5}$$

and

$$A^{(+)}=\frac{\hat{H}}{N+1}-\frac{(\hat{H}P+P\hat{H})}{2}+\frac{(VP+PV)}{2}-VG^{(+)}_{P}V. \tag{6}$$

In the above equations, $|S_{\vec{k}_i}\rangle$ is a product of a target state with a plane wave, i.e., it is a solution of the unperturbed Hamiltonian H_0. The interaction potential between the incident electron and the molecular target is given by V, and $\hat{H}=E-H$ is defined as the total energy of the collision E minus the full system Hamiltonian $H=H_0+V$. P is the projection operator for the energetically open electronic states of the target,

$$P=\sum_{l}^{\text{open}}|\phi_l\rangle\langle\phi_l|. \tag{7}$$

In the present case we will consider only the ground electronic state as energetically open, i.e., $P=|\phi_1\rangle\langle\phi_1|$. Finally, $G^{(+)}_{P}$ is the free-particle Green's function projected onto the P space.

As we mentioned before, our aim is to introduce a new set of configurations in place of the $|\chi_m\rangle$ and, as a consequence, to reduce the size of all matrices of Eq. (4). To start, let us consider the eigenstates $|\psi^{N+1}_{i}\rangle$ of the matrix formed by the full Hamiltonian written in the space of configurations $|\chi_m\rangle$, i.e., the matrix $H_{mn}=\langle\chi_m|H|\chi_n\rangle$. The space spanned by these eigenstates is exactly the same as the space spanned by the $|\chi_m\rangle$ configurations, i.e., the transformation $|\psi^{N+1}_{i}\rangle=\Sigma_m U_{im}|\chi_m\rangle$ is simply a rotation within the $|\chi_m\rangle$ space. We now consider the use of the eigenstates $|\psi^{N+1}_{i}\rangle$ to expand the scattering wave function $|\Psi^{(\pm)}_{(\vec{k})}\rangle$. If we use all the $|\psi^{N+1}_{i}\rangle$ eigenstates, we obtain the same result as if we use the $|\chi_m\rangle$ configurations. However, we propose to select a *subset* of all the $|\psi^{N+1}_{i}\rangle$ to expand the scattering wave function, and what we will show below is that this subset may be chosen to be *much smaller* than the full space spanned by all the $|\chi_m\rangle$. These eigenstates used in the expansion of the scattering wave function are what we call the effective configurations. The idea behind the use of the eigenstates of the full Hamiltonian is that, even though they may correspond to resonant states, and therefore would not be true bound states, they carry information about the interaction of the extra electron with the target within the range of the potential V, which is relevant for the scattering process at low incoming energies. One could say that some of these eigenstates may resemble the scattering wave function within the range of V.

Note that even though the diagonalization of the full Hamiltonian still involves all the $|\chi_m\rangle$ configurations, this is relatively simple when compared to the calculation of the scattering amplitude. Moreover, standard packages, like GAMESS [10], for example, can be used to perform this task.

The SMC method uses Cartesian Gaussian functions to represent the molecular and scattering orbitals, which permits the analytical evaluation of all matrix elements in Eq. (4), except those in the $\langle\chi_m|VG^{(+)}_{P}V|\chi_n\rangle$ term, which are evaluated by a numerical quadrature [11]. The basis functions were selected to reproduce well the H_2 polarizability and the elastic integral cross section. They are composed of $6s$ functions (exponents 39.186 359, 6.567 806 2, 1.774 537 5, 0.623 416 8, 0.235 659, 0.089 189 0) and $4p$ functions (exponents 5.6, 1.4, 0.178 571, 0.05) centered on the H atoms, and $2d$ functions (exponents 0.041 835, 0.011 785) centered in the middle of the H-H bond. The values obtained for the polarizability components parallel and perpendicular to the molecular axis are 6.45 a.u. and 4.59 a.u., respectively. The calculations were performed using the finite field method [10], and these values are in good agreement with other theoretical calculations [12,13]. With these basis functions we can generate a total of 2021 configurations to be used in the expansion of the scattering wave function. This defines the full space of $|\chi_m\rangle$ configurations discussed above.

To select which EC's to include, we use two criteria. (i) We first select the configurations based on the energies of the EC's relative to the ground state energy of the neutral molecule (E_0). The energies E_{EC} of the EC's are simply the eigenvalues of the $N+1$ Hamiltonian matrix, and when we say that a cutoff of E_{cut} was used, this means that all the EC's with E_{EC} such that $E_{\mathrm{EC}}-E_0 \leqslant E_{\mathrm{cut}}$ *may* be used to expand the scattering wave function. Intuitively one would expect that the lowest energy eigenstates should be more important to expand the scattering wave function, and this is precisely what we find. (ii) From this set of configurations we are going to select a subset that is actually going to be used in the expansion of the scattering wave function. To make such a selection we use the diagonal elements of the $(PV+VP)$ matrix in the basis of eigenstates of the $N+1$ Hamiltonian. We choose another cutoff $(PV+VP)_{\mathrm{cut}}$ such that only the EC's that have an absolute value of the diagonal element larger than $(PV+VP)_{\mathrm{cut}}$ will be considered. The diagonal element of $PV+VP$ is the average value of this operator for a particular effective configuration. The operator P, defined in Eq. (7), is a projector onto the electronic open channel space and its presence defines the coupling level of the problem and carries the information that out of $N+1$ electrons, N are bound to the molecule. In the primitive configuration space, the $PV+VP$ operator has nonzero diagonal elements only among configurations constructed with target wave functions of P [those defined by Eq. (2)—the static-exchange type of configurations]. On the other hand, in the effective configuration space [combination of open and closed channel type of configurations defined by Eqs. (2) and (3)], 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 contribute to 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 [14]). If we only use the energy criterion we include states that have low energy but have small overlap with the scattering potential, which, as shown below, may introduce numerical instabilities in the calculation [a near zero in the denominator of the scattering amplitude, given by Eq. (4)]. The $PV+VP$ criterion eliminates this kind of state and chooses trial configurations with strong coupling between open-open and open-closed channels. This criterion further decreases the size of the trial basis space.

In Fig. 1 we present the integral cross section decomposed by symmetry. We show the results for ${}^2\Sigma_g$, ${}^2\Sigma_u$, and ${}^2\Pi_u^+$ global symmetry. For each symmetry we present (i) the results using all possible configurations for that given symmetry (we name it the full calculation); (ii) the results with all configurations that satisfy the criterion (i) of the previous paragraph for E_{cut} = 20 eV (this value is used because it is the smallest possible value of E_{cut} that gives good results for the cross sections when compared to the full calculation); (iii) the results using the configurations from a subset from (ii) using $(PV+VP)_{\mathrm{cut}}=10^{-4}$. First of all, it is important to stress that the same criteria of selection of configurations are

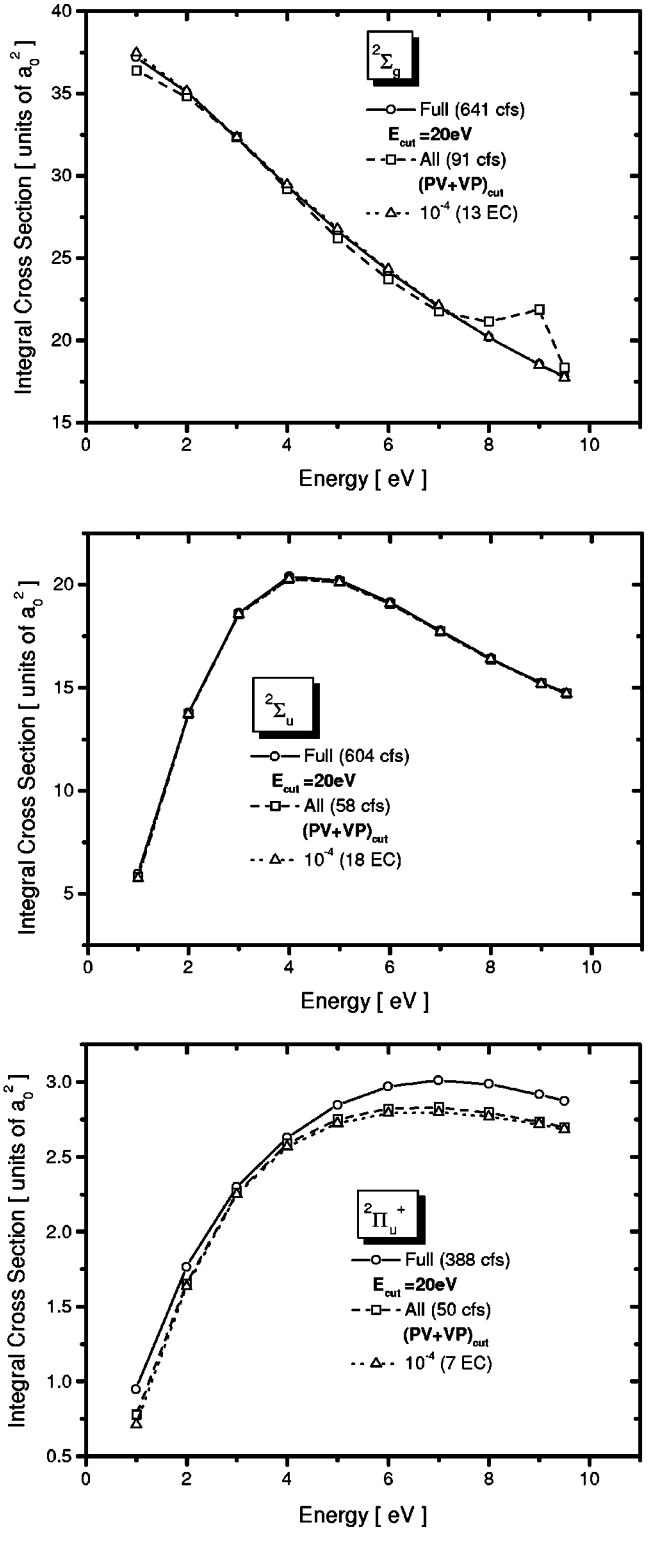

FIG. 1. Symmetry resolved integral cross section. Comparison of our present calculated results. Open circles: full configuration space; open squares: with $E_{\mathrm{cut}}=20$ eV; open triangles: with $E_{\mathrm{cut}}=20$ eV and $(PV+VP)_{\mathrm{cut}} \geqslant 10^{-4}$.

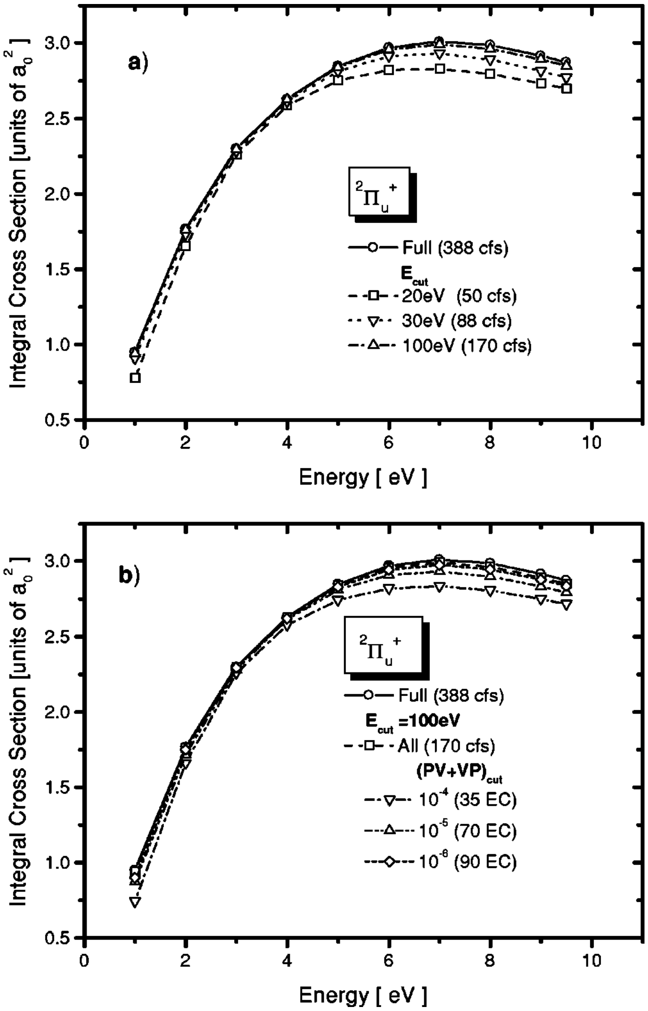

FIG. 2. $^2\Pi^+$ symmetry cross section. Comparison of our present result using (a) different E_{cut}'s and (b) different $(PV+VP)_{\mathrm{cut}}$'s for $E_{\mathrm{cut}}=100$ eV.

being used for all the symmetries. Second, one should note that even though the results using only the energy cutoff criterion seem to be already converged to the full calculation, it may lead to spurious structures in the cross sections (see the results for the $^2\Sigma_g$ symmetry). However, when we use the $(PV+VP)_{\mathrm{cut}}$ criterion we not only reduce the number of configurations (which in itself is very desirable), but also eliminate all the spurious structures. As can be seen already from these results, we can reproduce the full calculation with only a small number of configurations, of the order of 2–3 % of the total number of configurations for each symmetry.

From Fig. 1, one can see that the $^2\Pi_u^+$ symmetry is not as well converged as the other symmetries. Therefore we present a more detailed analysis for this symmetry, which is shown in Fig. 2. We first show the convergence of the integral cross section toward the full calculation as a function of E_{cut}. For $E_{\mathrm{cut}}=100$ eV the result is already indistinguishable from the full calculation. One should note that by only using E_{cut} to select the EC's, the necessary number of configurations is already only 44% of the total number of configurations for this symmetry. For $E_{\mathrm{cut}}=100$ eV, we further studied the effect of $(PV+VP)_{\mathrm{cut}}$. For $(PV+VP)_{\mathrm{cut}}=10^{-6}$ we reach a limit where the result is indistinguishable from the full calculation, but using only 23% of the total number of configurations for this symmetry. Therefore, we show that by changing both the E_{cut} and the $(PV+VP)_{\mathrm{cut}}$ criteria, we have a systematic way of improving the convergence toward the full calculation, but still keeping the total number of required EC's much smaller than the full configurational space.

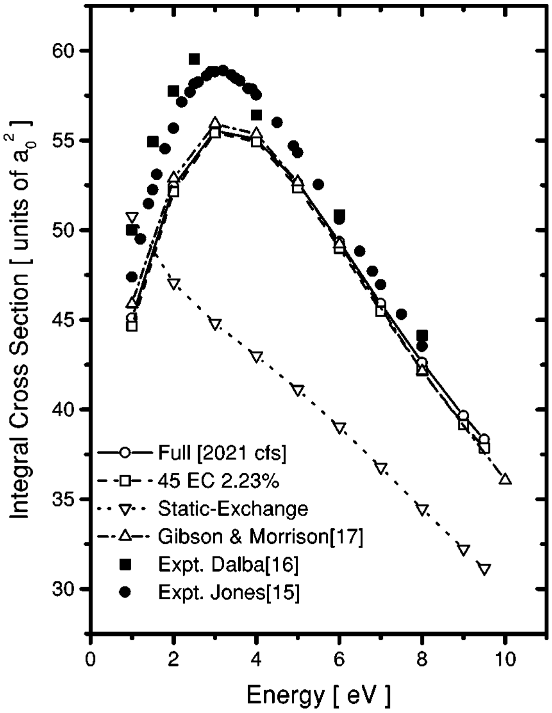

FIG. 3. Elastic integral cross section. Open circles: present results using the full configuration space (2021 configurations); open squares: present results using 45 effective configurations with $E_{\mathrm{cut}}=20$ eV and $(PV+VP)_{\mathrm{cut}}\geqslant 10^{-4}$; open down triangles: present static-exchange results; open up triangles: theoretical results of Ref. [17]; solid squares: experimental data of Ref. [16]; solid circles: experimental data of Ref. [15].

In Fig. 3 we present the elastic integral cross section calculated with all the 2021 configurations and with a selected set of EC's. When all the 2021 configurations are included, our results are in good agreement with the experimental data of Jones [15] and of Dalba *et al.* [16], and with the theoretical results of Gibson and Morrison [17], which gives us confidence in our basis functions. The EC's were selected using $E_{\mathrm{cut}}=20$ eV and $(PV+VP)_{\mathrm{cut}}=10^{-4}$, which gave a good agreement with the full calculation for the partial symmetry studies presented before. As can be seen, the results are in excellent agreement with the reference calculation. The total number of EC's used is 45 configurations, or in other words only 2.23% of all possible configurations. For comparison, we also present the cross sections calculated at the static-exchange level. The results at this level are very poor, which shows that polarization effects are very important to reproduce the experimental data. Therefore, the good agreement between theory and experiment with only 45 EC's is not a reflection of the lack of importance of polarization effects, but rather an indication that our choice of EC's is capturing the essential physics.

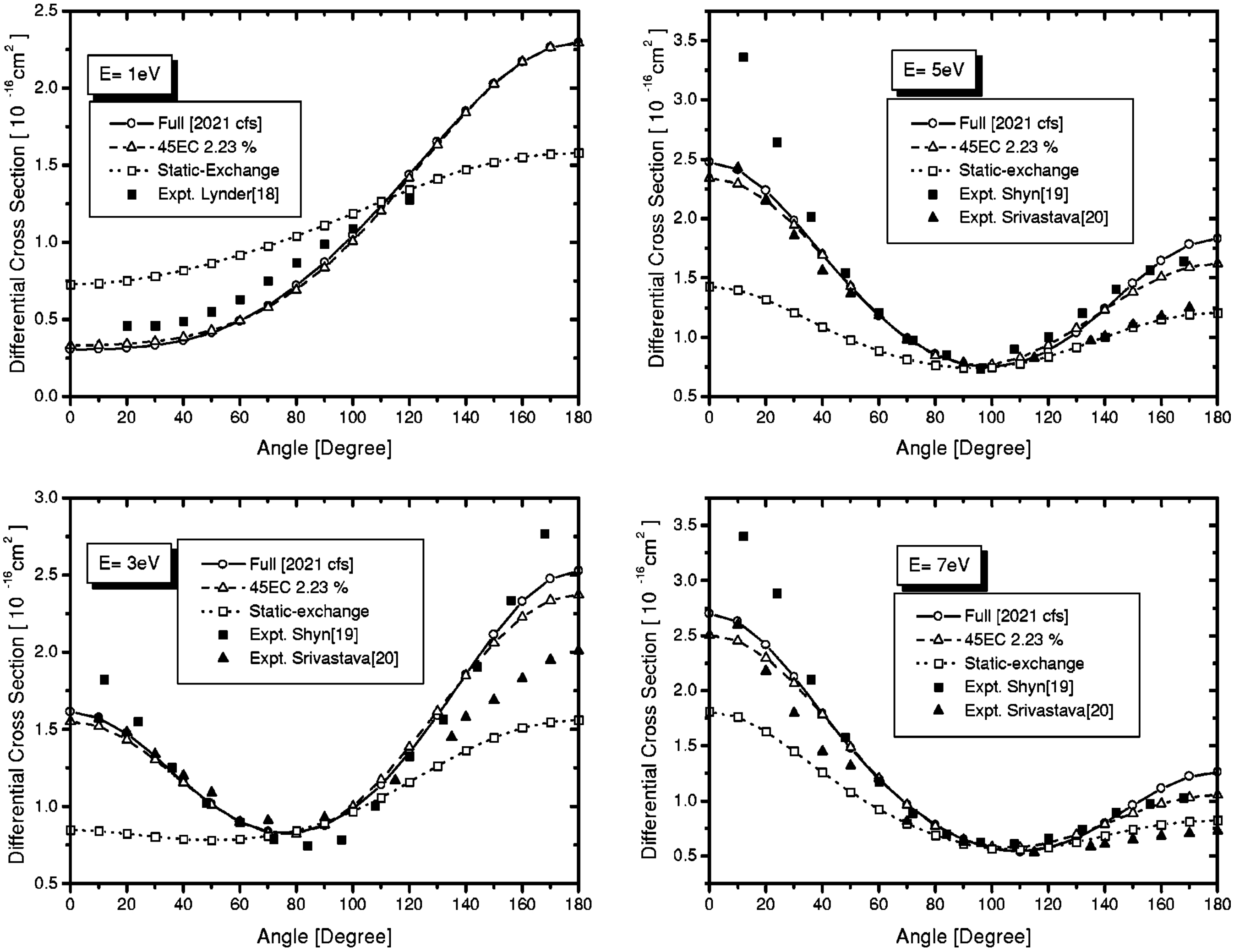

FIG. 4. Elastic differential cross sections at 1, 3, 5, and 7 eV. Comparison of our present results obtained with full configuration space (2021 configurations), with 45 effective configuration space, with the static-exchange level of approximation, and experimental data of Refs. [18], [19], and [20].

We also calculated differential cross sections, which are presented in Fig. 4 for incident energies of 1, 3, 5, and 7 eV. We present results with all 2021 EC's included, with only 45 EC's included, and also at the static-exchange level. For comparison we also include experimental results [18–20]. As can be seen, our reference calculation is in good agreement with the experimental results. Once more the static-exchange calculation gives a very poor agreement with the experimental results as well as with the reference calculation, which indicates that polarization effects are very important. Even at 7 eV one can see that polarization effects must be considered. As in the case of the integral cross section, the results with only 45 EC's already capture the important physics, which shows that only 2.23% of all configurations is already enough to describe well the polarization effects.

In conclusion, we have presented a method to calculate low energy electron-molecule scattering cross sections within the SMC method that is much more efficient when polarization effects are important. This method relies on the expansion of the scattering wave function in a set of functions of $N+1$ electrons which describe the important physics in an effective way, allowing the reduction of the configuration space of $N+1$ electrons by almost 98%. We have tested this methodology in the scattering of electrons by H_2 with great success, and more applications are under way.

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