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Studies of Electron–Molecule Collisions on Distributed-memory Parallel Computers*

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Abstract

We review recent progress in the study of low-energy collisions between electrons and polyatomic molecules which has resulted from the application of distributed-memory parallel computing to this challenging problem. Recent studies of electronically elastic and inelastic scattering from several molecular systems, including ethene, propene, cyclopropane, and disilane, are presented. We also discuss the potential of *ab initio* methods combined with cost-effective parallel computation to provide critical data for the modeling of materials-processing plasmas.

1. Introduction

Significant progress has been made during the last several years in the *ab initio* study of low-energy electron–molecule collision processes. There have been both developments in methodology (e.g., Collins and Schneider 1988; McCurdy *et al.* 1987; McNaughten and Thompson 1988) and developments in the application of existing methods. One of the most promising of the latter is the rise of distributed-memory parallel computers (Fox *et al.* 1988) as a tool for the theoretical study of problems in molecular physics (see e.g. Wu *et al.* 1990; Colvin *et al.* 1989). We have recently been engaged in implementing the Schwinger multichannel (SMC) method for electron–molecule collisions (Takatsuka and McKoy 1981, 1984) on several distributed-memory machines (Hipes *et al.* 1990, 1992), and in applying that implementation to the study of a number of interesting collision processes (Winstead *et al.* 1991, 1992; Sun *et al.* 1992). Here we wish to describe both the SMC method in its parallel implementation and some illustrative results of recent applications.

The objective of this ongoing research is the development of a theoretical approach which will make practical extensive studies of collisions between electrons and small polyatomic molecules. We are particularly interested in species such as SiH_4, Si_2H_6, CCl_4 and C_2F_4, whose collision cross sections are needed to model low-temperature plasmas used industrially in semiconductor manufacturing (see e.g. Manos and Flamm 1989), and we are also interested in various hydrocarbon species used in plasma-assisted chemical vapour deposition and plasma polymerisation (JTIS 1988). In such low-temperature plasmas, collisions

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between 'hot' electrons, with energies of the order of tens of eV (1 eV $\approx$ 12 000 K), and molecules, with thermal energies of the order of several hundred K, generate reactive fragments which can lead to chemical modification of surfaces, without the need for destructively high temperatures. Optimisation of the plasma's operating parameters is crucial, yet at present most optimisation must be done by trial and error, because the great complexity of the plasma as a physical system makes it difficult to relate desired properties to the operating conditions. Numerical modeling of such plasmas—a significant computational challenge in itself—holds promise for providing an understanding of plasma behaviour based on microscopic processes (IEEE 1991), but successful modeling depends on the existence of a database of collision cross sections for the important species that are present in actual applications. Since the relevant experimental data are in most cases fragmentary or nonexistent, and since many interesting species are highly reactive and indeed hazardous gases, difficult to study experimentally, there is a clear role for theory to play.

To reach our goal of establishing computation as a primary source of data for collisional plasma modeling requires both efficient theoretical methods and the use of the most cost-effective high-performance computers available. In the following we will describe the SMC method, with particular reference to those features which make it well suited for an implementation on distributed-memory parallel supercomputers, a class of machine which provides high absolute performance yet does so at very reasonable cost in comparison with conventional supercomputers. We will also describe aspects of the organisation of SMC calculations for concurrent execution. The remainder of the paper is devoted to presentation and discussion of a representative selection of recent results.

2. Method and Implementation

The Schwinger multichannel method is an extension of the variational principle for scattering problems introduced by Schwinger (1947). It preserves several desirable characteristics of the original principle—specifically, freedom from the requirement that basis functions satisfy scattering boundary conditions and rapid convergence—while possessing features desirable in electron–molecule scattering applications. Most important of these is the use of a projected Green's function (Takatsuka and McKoy 1981, 1984) whose representation does not require the (in general unknown) continuum states of the target molecule. Physical effects such as polarisation of the target and electron exchange that are important in low-energy scattering may be incorporated in a natural way, and electronically inelastic as well as elastic scattering may be considered. The method has been implemented in such a way that molecules of arbitrary geometry can be treated, and all matrix elements necessary to evaluate the variational expression are obtained in closed form, with the exception of those involving the Green's function. The latter are evaluated accurately via numerical quadrature (Lima *et al.* 1990). We return to these points below.

To see how the SMC formulation arises, we write the Hamiltonian for the $(N+1)$-electron system (target plus scattering electron) as

$$H = (H_N + T_{N+1}) + V = H_0 + V\,, \tag{1}$$

where H_N is the Hamiltonian of the target, T_{N+1} the kinetic-energy operator for the scattering electron, and V the target–scatterer interaction. Based on (1) we can write a Lippmann–Schwinger equation for the $(N+1)$-electron eigenstates $\Psi_m^{(\pm)}$:

$$\Psi_m^{(\pm)} = S_m + G_0^{(\pm)} V \Psi_m^{(\pm)}, \tag{2}$$

with

$$S_m = \Phi_m(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \exp(i\boldsymbol{k} \cdot \boldsymbol{r}_{N+1}) \tag{3}$$

being the interaction-free solution, i.e., the eigenstate of H_0, and $G_0^{(\pm)}$ the corresponding Green's function; in (3) the state Φ_m is the target state for channel m,

$$H_N \Phi_m = E_m \Phi_m. \tag{4}$$

Since $\Psi_m^{(\pm)}$ is fully antisymmetric and S_m is not, it is clear from (2) that continuum states of the target are required in the representation of G_0, as has been emphasised by Geltman (1969). This is a serious difficulty since the continuum states of the N-electron target will in general be no better known than the $(N+1)$-electron functions $\Psi_m^{(\pm)}$. To remove this obstacle, we introduce a projection operator P which selects only open channels (assumed to exclude ionisation channels),

$$P = \sum_{\ell \text{open}} |\Phi_\ell(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\rangle \langle \Phi_\ell(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|, \tag{5}$$

and apply this projector to the Lippmann–Schwinger equation (2):

$$P\Psi_m^{(\pm)} = S_m + G_P^{(\pm)} \Psi_m^{(\pm)}. \tag{6}$$

The complementary portion of $\Psi_m^{(\pm)}$, i.e. $(1 - aP)\Psi_m^{(\pm)}$ for a a constant (to be fixed later), may be recovered by requiring (Lima and McKoy 1988) that the two components of $\Psi_m^{(\pm)}$ together satisfy Schrödinger's equation:

$$(E - H)\{aP\Psi_m^{(\pm)} + (1 - aP)\Psi_m^{(\pm)}\} = 0. \tag{7}$$

Substitution of the projected Lippmann–Schwinger equation (6) for $P\Psi_m^{(\pm)}$ and some straightforward rearrangement leads to

$$A^{(\pm)} \Psi_m^{(\pm)} = V S_m, \tag{8}$$

with $A^{(\pm)}$ given by

$$A^{(\pm)} = \tfrac{1}{2}(PV + VP) - V G_P^{(\pm)} V - \tfrac{1}{2}(P\hat{H} + \hat{H}P) + \tfrac{1}{a}\hat{H}, \tag{9}$$

where $\hat{H} = E - H$. A variational functional for the scattering amplitude f_{mn} may now be based on (8):

$$f_{mn} = -\frac{1}{2\pi}\left(\langle S_m|V|\Psi_n^{(+)}\rangle + \langle\Psi_m^{(-)}|V|S_n\rangle - \langle\Psi_m^{(-)}|A^{(+)}|\Psi_n^{(+)}\rangle\right), \tag{10}$$

provided that the condition

$$A^{(-)\dagger} = A^{(+)} \tag{11}$$

is satisfied, which in turn requires $a = N+1$ (Takatsuka and McKoy 1981, 1984). With this value of a, it also becomes possible to employ a purely L^2 expansion of the wave function, greatly facilitating numerical studies.

In actual applications, the scattering wave function is typically expanded in a set of $(N+1)$-electron spin-adapted Slater determinants of one-electron functions. For numerical convenience, the one-electron functions are chosen to be combinations of the Cartesian Gaussian orbitals commonly used in electronic structure studies. With this choice, all matrix elements needed to construct the variational functional are obtainable in closed form, except those involving the Green's function. These $VG_P^{(+)}V$ matrix elements are evaluated instead through a numerical quadrature in the momentum variable occurring in the spectral representation of the Green's function (Lima *et al.* 1990). The choice of $(N+1)$-electron functions determines the type of calculation being undertaken. For example, elastic scattering within the static-exchange approximation requires only determinants arising from the addition of one orbital to the N-electron ground state configuration. To include polarisation, configurations which are single excitations from the ground state plus an additional orbital would be included in the expansion of $\Psi_m^{(\pm)}$ but omitted from the projector P, thereby introducing the effect of closed excitation channels. Electronic excitation is treated by designating certain excitations as open channels and including the appropriate configurations in P as well as in the expansion of the wave function.

The SMC formulation described above has been successfully applied to a number of diatomic and small polyatomic targets in the past several years (see e.g. Lima *et al.* 1988; Pritchard *et al.* 1990; Winstead and McKoy 1990). However, the species of interest in plasma-processing applications are typically polyatomic molecules containing several heavy (i.e. non-hydrogen) atoms, and accurate calculations for these larger species can be quite 'compute-intensive'. For this reason, we were led to consider implementing the method on distributed-memory parallel computers, which provide performance matching or exceeding that of conventional supercomputers in a cost-effective fashion.

While there is much variation in the architecture of parallel computers, the machines with which we have experience share the same general characteristics. Each consists of a large number of microprocessor-based computing elements, or nodes. These nodes operate autonomously; at any given moment they may or may not be executing the same instructions. Such a machine is referred to as a multiple-instruction-stream, multiple-data-stream, or MIMD, computer. (In contrast, another important category, which includes the well-known Connection Machine, is single-instruction, multiple-data, or SIMD, in which all processors execute the same instructions in lock-step.) The term 'distributed-memory' refers

to the fact that each node has access only to its own local storage; data residing on one node that are needed on another must be explicitly communicated. This communication takes place over a network of channels typically of hypercube or mesh topology. The high performance of such a machine arises from the division of labour among many relatively slow, inexpensive microprocessors which can be adequately supported by relatively slow memory. In contrast, the high performance of conventional supercomputers is achieved through the use of a few extremely fast central processors sharing a common fast memory. Aside from the ultimate technological limitations (due, for instance, to the finite speed of light) upon the conventional approach, its reliance on 'state-of-the-art' components places it at a significant cost disadvantage, which is likely to grow as microprocessor technology advances.

It is not difficult to see that the SMC method is suitable for implementation on distributed-memory MIMD multiprocessors. The computationally intensive step in the method is evaluation of large numbers of two-electron integrals

$$\langle \alpha\beta | \frac{1}{r_{12}} | \gamma \boldsymbol{k} \rangle = \int\int d^3r_1 d^3r_2 \alpha(\boldsymbol{r}_1)\beta(\boldsymbol{r}_1)\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\gamma(\boldsymbol{r}_2)\exp(i\boldsymbol{k}\,.\,\boldsymbol{r}_2)\,, \qquad (12)$$

where α, β and γ are Cartesian Gaussian functions. These integrals, which arise both in the terms $\langle S_m | V | \Psi_n^{(+)} \rangle$ and $\langle \Psi_m^{(-)} | V | S_n \rangle$ of equation (10) and in the numerical quadrature evaluation of the Green's function term, are needed for all unique combinations of Cartesian Gaussians and for a wide range of directions and magnitudes of $\boldsymbol{k}$. Since the integrals can be evaluated independently, a natural strategy for parallelising this key step is to assign each processor the task of computing a different subset of the integrals. Thus, we load on each node a copy of the integral-evaluation subroutines (approximately 2000 lines of FORTRAN) and proceed to accumulate a subset of the integrals in each node's memory. Integrals involving different types of Cartesian Gaussians will take varying amounts of time to compute, and different steps will be followed in computing them; here a MIMD, rather than SIMD, architecture is clearly preferable. Load balance is achieved statistically: the number of integrals in any given batch vastly exceeds the number of nodes, so differences in integral computation time tend to average out if the integrals are divided equally and essentially randomly among the nodes.

To be useful, the one- and two-electron integrals must be transformed into appropriate combinations to yield the matrix elements occurring in (10). This transformation, which necessarily involves communication among the nodes, is efficiently and compactly coded in the form of a distributed matrix multiplication. A similar strategy is invoked to perform certain numerical integrations which likewise require interprocessor communication. The simplicity of this communication strategy has the added benefit of enhancing the portability of the program to new architectures. Remaining steps of the calculation are quite straightforward, with additional communication required only in the final stage, where a set of linear equations is solved with a distributed LU-factorisation scheme (Hipes 1989) and the solution used to generate the scattering amplitude.

At present our distributed-memory SMC program runs on three types of computers. It was originally written for the Mark III^{fp} developed at the Jet

Propulsion Laboratory, a hypercube-connected computer with up to 128 nodes, each with a 64-bit peak speed of approximately 14 MFlop (14×10^6 floating-point operations/second) and 4 Mbyte of memory. We have since ported the program to the Intel Touchstone GAMMA and DELTA architectures, which are both based on the 60-MFlop i860 microprocessor. The GAMMA, commercialised as the iPSC/860, is also a hypercube, with up to 128 nodes; the machine at Caltech has 64 nodes, each with 16 Mbyte memory. The DELTA, a unique prototype machine recently delivered to the Concurrent Supercomputing Consortium led by Caltech, is a mesh-connected multiprocessor with 520 i860 processing elements (of which up to 512 can be allocated to a single job), each having 16 Mbyte memory. We are still engaged in optimisation of the program for the Intel computers; performance on the DELTA is approximately 1 GFlop at present, inclusive of all overhead. We anticipate that this figure will improve substantially with further optimisation and with improvements in the compilers and libraries.

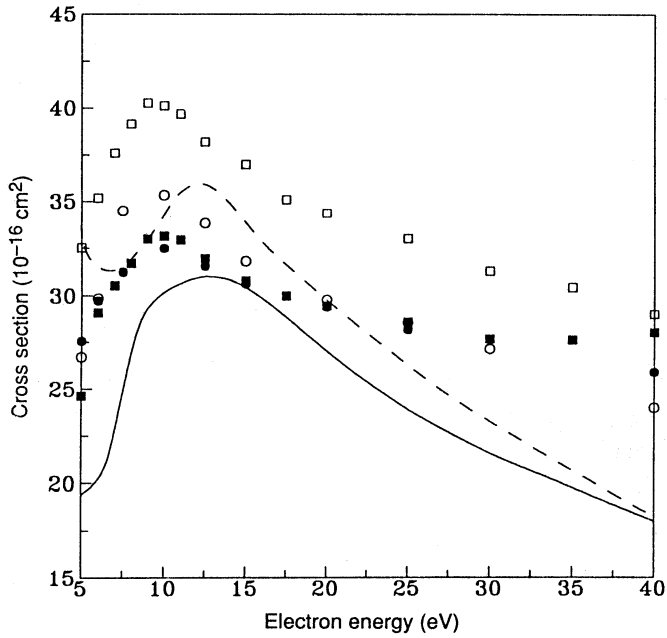

Fig. 1. Calculated integral cross sections for elastic scattering of electrons by cyclopropane (solid curve) and propene (dashed curve). Experimental total cross sections (circles, Floeder *et al.* 1985; squares, Nishimura and Tawara 1991) are also shown, with filled symbols representing cyclopropane and open symbols propene data.

3. Selected Results

In this section we present a few results of recent calculations (Sun *et al.* 1992; Winstead *et al.* 1991, 1992) which illustrate the types of problems and applications in which we are interested. Where possible we show experimental data to allow for comparison.

Fig. 1 shows integral elastic cross sections for the C_3H_6 isomers cyclopropane and propene (Winstead *et al.* 1992). These were calculated within the fixed-nuclei

static-exchange approximation as one of the initial applications of our program on the DELTA. Since the calculation omits polarisation effects, we do not expect quantitative results at the lower energies, where those effects are most important; further, maxima in the cross section will generally be shifted by approximately 1–3 eV to higher energy and somewhat broadened. When these limitations are borne in mind such calculations may nevertheless be quite useful.

To our knowledge there exist no experimental or other theoretical data on elastic scattering by these molecules; however, measurements of the total scattering cross section have been reported (Floeder *et al.* 1985; Nishimura and Tawara 1991), and we show these in Fig. 1. At the higher energies the measurements may include substantial contributions from electronically inelastic scattering processes, but at lower energies elastic scattering will predominate. As may be seen, overall agreement between experiment and theory is reasonable out to approximately 20 eV. The calculation indicates a fairly pronounced isomer effect near the cross section maximum, in agreement with the experiment of Nishimura and Tawara, and suggests that the propene cross section may be underestimated by Floeder *et al.*, particularly when allowances are made for the effects of omitting polarisation that were mentioned above.

An interesting feature of the scattering from cyclopropane that is not readily apparent from Fig. 1 is the presence of a shape resonance, placed by the calculation at about 8·5 eV and thus likely to be found near 6 eV in actuality. A partial-wave analysis shows that this resonance appears in A_2' symmetry, and it can be associated with a virtual valence orbital which is a completely out-of-phase combination of carbon $2p$ orbitals. It is related to the well-known π^* shape resonance of alkenes (e.g. Jordan and Burrow 1980) but contains a significant admixture of σ^* character, accounting for its unusually high energy. In Fig. 1, this resonance accounts for the rapid rise on the low-energy side of the broad maximum in the cyclopropane integral elastic cross section. Its influence is much more readily seen in the differential cross section at 8 eV, Fig. 2, where it produces oscillation at intermediate angles not seen in propene, and it might also be expected to influence vibrational-excitation cross sections.

Further examples of work done in the static-exchange approximation are given in Fig. 3, where we show momentum-transfer cross sections for three species of interest in semiconductor manufacturing, namely germane (GeH_4), silane (SiH_4) and disilane (Si_2H_6) (Winstead and McKoy 1990; Winstead *et al.* 1991). While the shapes of the cross sections in the energy range studied are not especially interesting, data of this sort are nonetheless quite useful in technological applications (as discussed e.g. in Hayashi 1987). Comparison with experiment (Tanaka *et al.* 1990) is possible for silane, and agreement is quite good. Although an experimental momentum-transfer cross section for disilane is not available, the differential cross section, on which it depends, has been measured (Tanaka *et al.* 1989) and agrees very well with our calculation. Recent experimental work on germane (M. A. Dillon, personal communication 1990) has indicated that the forward scattering is considerably stronger than indicated by our calculation; however, even if this is the case, there should be little effect on the momentum-transfer cross section, which emphasises the scattering at high angles where agreement is much better.

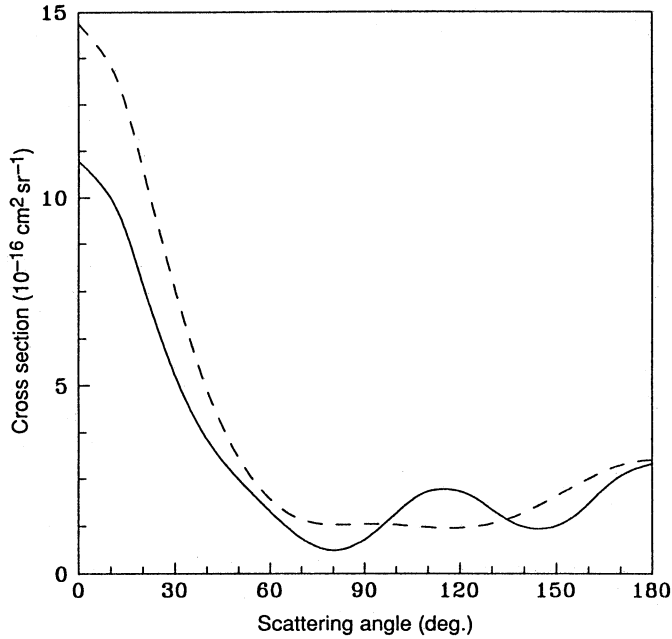

Fig. 2. Calculated differential cross sections for scattering of 8 eV electrons by cyclopropane (solid curve) and propene (dashed curve).

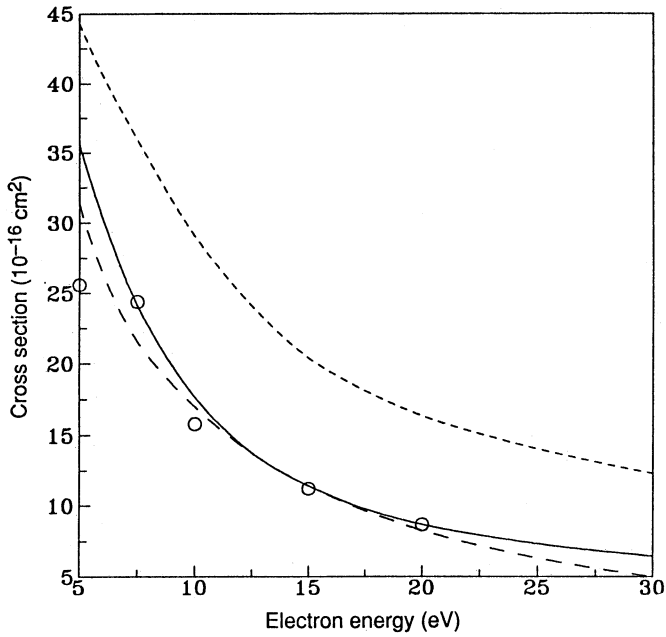

Fig. 3. Theoretical momentum-transfer cross sections for electron collisions with silane (solid curve), disilane (short-dashed curve), and germane (long-dashed curve). Experimental values for silane (Tanaka *et al.* 1990) are shown as circles.

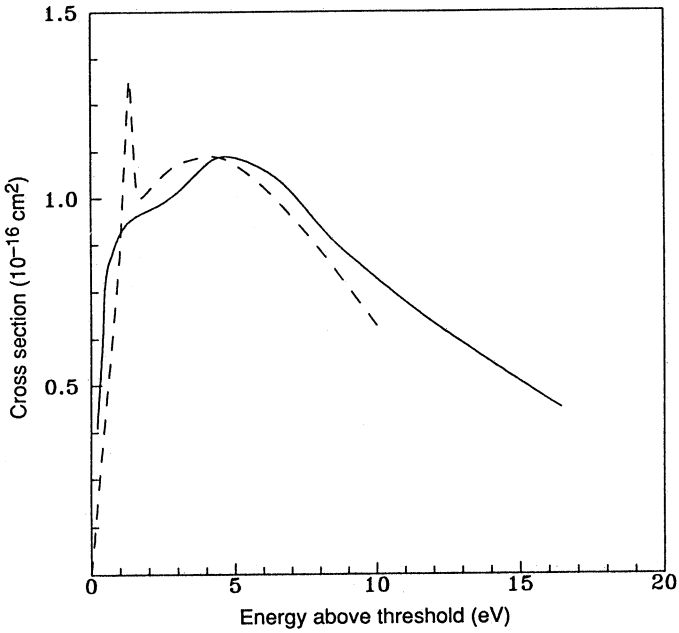

Fig. 4. Integral cross section for electron-impact excitation of the $a\ ^3B_{1u}$ state of ethene. Calculated results are shown as the solid curve; trapped-electron measurements (van Veen 1976), normalised to the calculation at the broad maximum, are shown by the dashed curve.

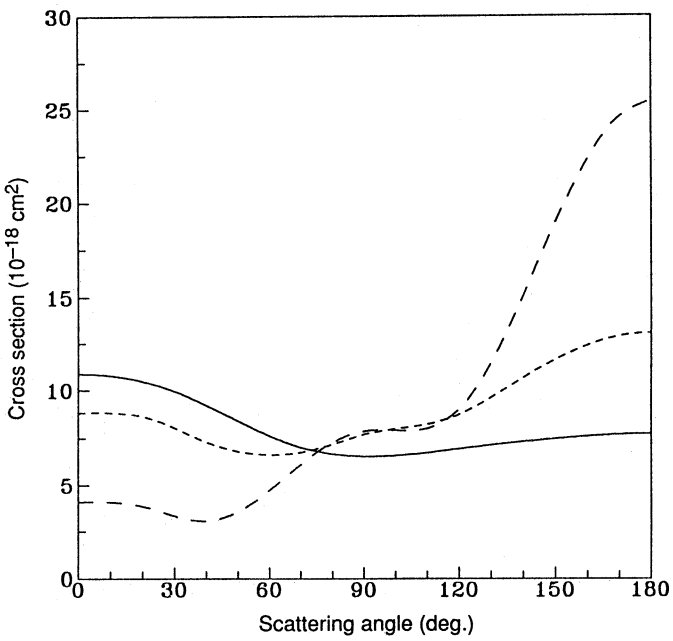

Fig. 5. Calculated differential cross sections for scattering of electrons which have excited the $a\ ^3B_{1u}$ transition in ethene at 1·4 eV (solid curve), 3·4 eV (short-dashed curve) and 6·4 eV (long-dashed curve) above threshold.

Collisions leading to excitation or dissociation of the target are naturally of particular interest in low-temperature plasma modeling, and we have calculations in progress for several systems. Results of recently completed work on the $(\pi \rightarrow \pi^*)$ $a\ ^3B_{1u}$ excitation of ethene (C_2H_4) are shown in Figs 4 and 5. The integral excitation cross section, Fig. 4, rises rapidly to a shoulder at approximately 1·4 eV above threshold, which is followed by a broad maximum and a slow decline. Fig. 4 includes the excitation function for this transition measured by van Veen (1976) using the trapped-electron technique; we have normalised his relative measurement to our value at the broad maximum. The experiment indicates a narrow feature approximately 1·3 eV above threshold, which van Veen has interpreted as a $\pi(\pi^*)^2$ core-excited shape resonance. Analysis of the calculated scattering amplitude indicates that the shoulder at 1·4 eV is due to a sharp maximum in the contribution of the incoming $\ell = 2$, $m = \pm 1$ partial wave, which is not consistent with an interpretation of this feature as a $\pi(\pi^*)^2$ resonance. A recent complex-Kohn calculation (Rescigno and Schneider 1992) of the same cross section, while showing a sharp structure reminiscent of that in the experiment, attributes that structure to the tail of the elastic-channel shape resonance. Further work will be needed to clarify the situation.

Differential cross sections for the $a\ ^3B_{1u}$ excitation are shown in Fig. 5. At low energies the cross section is rather isotropic, with some slight enhancement in the forward and backward directions. As the energy increases the backward peaking characteristic of exchange-mediated excitation processes quickly appears. Relevant experimental data (Trajmar *et al.* 1970) are extremely limited and not directly comparable, but are at any rate not inconsistent with the calculated results.

4. Discussion and Conclusion

The progress that has recently been made in the theoretical study of collisions between low-energy electrons and polyatomic molecules is highly encouraging. *Ab initio* calculations at the static-exchange level for small polyatomics are fairly routine and provide useful semiquantitative data. With some additional numerical effort, it is quite straightforward to include polarisation effects if more accurate results are required, at least below the first electronic threshold. Elastic scattering studies for systems larger than those discussed above, such as CF_4 and SiF_4, are under way in our group at present; studies of still larger systems are quite feasible, although technical improvements to the sequential portion of the program (specifically the four-index transformation in the electronic-structure package) will eventually be required.

At the same time, if theory is to be a significant contributor of essential collision data, much remains to be done. Calculations of electronic excitation cross sections in particular remain scarce. Although such calculations are within the capabilities of several current theoretical approaches, including the SMC method, and results are beginning to appear with some regularity, experience has proven that calculations of inelastic scattering are considerably more demanding than calculations of elastic scattering. Special care must be taken in the choice of a one-electron basis set and in the representation of the target states, and physical insight must usually be applied in choosing which channels are to be

included in a feasible calculation. Just what the essential ingredients of a reliable calculation are and to what extent they depend on the nature of the excitation process under study are in fact questions only beginning to be explored. The availability of extremely powerful, reasonably priced parallel computers greatly facilitates the extensive and detailed numerical study required to address these questions, as well as making possible calculations which would not otherwise have been feasible due to the size of the basis set or the number of channels included. We are at present engaged in the study of excitation processes in molecules including methane (CH_4), silane, formaldehyde (H_2CO) and acetone ($(CH_3)_2CO$), with a view both to providing useful results and to gaining further insight into the requirements of a reliable calculation.

Acknowledgments

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References

Collins, L. A., and Schneider, B. I. (1988). *In* 'Electronic and Atomic Collisions' (Eds H. B. Gilbody *et al.*), (North-Holland: Amsterdam).

Colvin, M. E., Whiteside, R. A., and H. F. Schaefer III (1989). *In* 'Methods in Computational Chemistry, Vol. 3: Concurrent Computation in Chemical Calculations' (Ed. S. Wilson), p. 167 (Plenum: New York).

Floeder, K., Fromme, D., Raith, W., Schwab, A., and Sinapius, G. (1985). *J. Phys.* B **18**, 3347.

Fox, G., Johnson, M., Lyzenga, G., Otto, S., Salmon, J., and Walker, D. (1988). 'Solving Problems on Concurrent Processors, Vol. I: General Techniques and Regular Problems' (Prentice-Hall: Englewood Cliffs).

Geltman, S. (1969). 'Topics in Atomic Collision Theory', p. 95ff (Academic: New York).

Hayashi, M. (1987). *In* 'Swarm Studies and Inelastic Electron Molecule Collisions' (Eds L. C. Pitchford *et al.*), p. 167 (Springer: New York).

Hipes, P. G. (1989). Comparison of LU and Gauss-Jordan system solvers for distributed memory multicomputers. Caltech Concurrent Computation Program Report C^3P-652b.

Hipes, P., Winstead, C., Lima, M., and McKoy, V. (1990). Proc. Fifth Distributed Memory Computing Conference, Vol. I: Applications (Eds D. W. Walker and Q. F. Stout), IEEE Computer Society, Los Alamitos, p. 498.

Hipes, P. G., Winstead, C., Sun, Q., Lima, M. A. P., and McKoy, V. (1992). *In* 'Parallel Computing Works' (Eds G. C. Fox *et al.*) (Morgan and Kaufman: San Mateo) (in press).

IEEE (1991). *IEEE Trans. Plasma Sci.* **19**, no. 2, 'Special Issue on Modelling Collisional Low-Temperature Plasmas'.

Jordan, K. D., and Burrow, P. D. (1980). *J. Am. Chem. Soc.* **102**, 6882.

JTIS (1988). 'Plasma Reactions and Their Applications', Japan Materials Report by Japan Technical Information Service, ASM International, Metals Park, Ohio, U.S.A.

Lima, M. A. P., Brescansin, L. M., da Silva, A. J. R., Winstead, C., and McKoy, V. (1990). *Phys. Rev.* A **41**, 327.

Lima, M. A. P., Gibson, T. L., McKoy, V., and Huo, W. M. (1988). *Phys Rev.* A **38**, 4527.

Lima, M. A. P., and McKoy, V. (1988). *Phys. Rev.* A **38**, 501.

McCurdy, C. W., Rescigno, T. N., and Schneider, B. I. (1987), *Phys. Rev.* A **36**, 2061.

McNaughten, P., and Thompson, D. G. (1988). *J. Phys.* B **21**, L703.

Manos, D. M., and Flamm, D. L. (Eds) (1989). 'Plasma Etching: An Introduction' (Academic: San Diego).
Nishimura, H., and Tawara, H. (1991). *J. Phys.* B **24**, L363.
Pritchard, H. P., McKoy, V., and Lima, M. A. P. (1990). *Phys. Rev.* A **41**, 546.
Rescigno, T. N., and Schneider, B. I. (1992). *Phys. Rev.* A **45**, 2894.
Schwinger, J. (1947). *Phys. Rev.* **72**, 742.
Sun, Q., Winstead, C., McKoy, V., and Lima, M. A. P. (1992). *J. Chem. Phys.* **96**, 3531.
Takatsuka, K., and McKoy, V. (1981). *Phys. Rev.* A **24**, 2473.
Takatsuka, K., and McKoy, V. (1984). *Phys. Rev.* A **30**, 1734.
Tanaka, H., Boesten, L., Sato, H., Kimura, M., Dillon, M. A., and Spence, D. (1989). 42nd Gaseous Electronics Conference, Palto Alto, Calif., U. S. A., p. 78, and personal communication.
Tanaka, H., Boesten, L., Sato, H., Kimura, M., Dillon, M. A., and Spence, D. (1990). *J. Phys.* B **23**, 577.
Trajmar, S., Rice, J. K., and Kuppermann, A. (1970). *Adv. Chem. Phys.* **18**, 15.
van Veen, E. H. (1976). *Chem. Phys. Lett.* **41**, 540.
Winstead, C., Hipes, P. G., Lima, M. A. P., and McKoy, V. (1991). *J. Chem. Phys.* **94**, 5455.
Winstead, C., and McKoy, V. (1990). *Phys. Rev.* A **42**, 5357.
Winstead, C., Sun, Q., and McKoy, V. (1992). *J. Chem. Phys.* **96**, 4246.
Wu, Y. S. M., Cuccaro, S. A., Hipes, P. G., and Kuppermann, A. (1990). *Chem. Phys. Lett.* **168**, 429.

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