

# Quantum-mechanical calculations of cross sections for electron collisions with atoms and molecules

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## Abstract

An overview of quantum-mechanical methods to generate cross-section data for electron collisions with atoms and molecules is presented. Particular emphasis is placed on the time-independent close-coupling approach, since it is particularly suitable for low-energy collisions and also allows for systematic improvements as well as uncertainty estimates. The basic ideas are illustrated with examples for electron collisions with argon atoms and methane. For many atomic systems, such as e-Ar collisions, highly reliable cross sections can now be computed with quantified uncertainties. On the other hand, while electron collision calculations with molecules do provide key input data for plasma models, the methods and computer codes presently used require further development to make these inputs robust.

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## I. INTRODUCTION

Electron collisions with atoms, ions, and molecules are well known to be of critical importance in the understanding and the modeling of laboratory and technological plasmas, astrophysical processes, lasers, and planetary atmospheres — to name just a few examples. Since the principal motivation of benchmark experiments in this field has been the test of theoretical models in as much detail as possible, without averaging, for example, over unpolarized initial beams and summing or integrating over unresolved observables in the final state, many of these experiments produce data that are differential in energy, angle, and even the spin of the particles involved. On the other hand, plasma modelers often need angle-integrated cross sections over extended energy ranges to calculate the relevant rate coefficients, sometimes resolved for particular initial and final states and sometimes just lumped over a number of possibilities. Of particular importance, however, is the need for *absolute* cross sections, which are notoriously difficult to obtain in experimental setups, especially in state-to-state resolved transitions involving neutral targets. Some information and additional references can be found in [1].

Furthermore, state-of-the art plasma modeling often requires data for a very large number of atomic and molecular processes [2]. It is virtually impossible to determine all the quantities needed by experimental means. The reason is not just the cost involved, but rather the fact that certain cross sections, which may be important in simulations of particular plasma environments, are not accessible to standard crossed-beam or gas-cell setups. Examples include transitions between excited states, especially if the initial state is not even metastable, and essentially all collisional data involving open-shell molecules, which are generally known as radicals. As a result, plasma modelers increasingly rely on theoretical predictions, rather than on educated guesses for the relevant cross sections and rate coefficients.

In light of the enormous progress made in both computational hardware and software, it has indeed become possible to generate a large amount of the required data by numerical means, and the results are typically collected in databases. Some information can be found in [3, 4]. Interestingly, the concept of uncertainty estimates, i.e., an assessment of the reliability of particular theoretical predictions, has only recently drawn significant attention among both data users and data producers. While the publishers of experimental data are routinely expected to provide some uncertainty estimates (as difficult as this may be for

systematic errors), this has not been a widely practiced tradition for theorists [5].

The present manuscript is organized as follows. We begin with a brief overview of quantum-mechanical methods developed for electron collisions with atoms and molecules, before concentrating on the time-independent close-coupling (CC) approach, which has been extensively used to obtain data for low-energy and more recently also for intermediate-energy collisions. After illustrating the basic ideas for electron-atom scattering, the extensions needed to handle molecular targets are outlined. The effect of various approximations, their advantages and shortcomings, are then illustrated for electron collisions with argon atoms and methane. Unless mentioned otherwise, atomic units are used throughout this paper.

## II. OVERVIEW OF NUMERICAL APPROACHES

There is a wealth of literature available on methods for electron scattering calculations. Instead of repeating this information in great detail, only the minimum framework needed for understanding the basic ideas will be presented here. For a more thorough treatment and overviews, standard textbooks on collision theory and recent reviews [6–10] should be consulted. Some descriptions and example computer programs for atomic structure and collisions can be found in [11]. In this paper, we will illustrate the basic principles on a few concrete examples that are well known to be important for plasma applications.

Unfortunately, there is no unambiguous rule regarding the reliability of a particular method. Nevertheless, as will be discussed further below, the collision energy is an important parameter that can provide some general guidelines. More details, in particular with regard to estimating the uncertainty and the reliability of theoretical predictions, can be found in [12].

Numerical approaches for atomic collision processes, and in particular for electron-atom and electron-molecule collisions, are often classified as perturbative or non-perturbative, as well as time-dependent or time-independent. Time-dependent formulations are based on the time-dependent Schrödinger equation (TDSE),

$$i\frac{\partial}{\partial t}|\Psi(\mathbf{X}, t)\rangle = H(\mathbf{X}, \mathbf{P}, t)|\Psi(\mathbf{X}, t)\rangle. \quad (1)$$

for the wavefunction  $|\Psi(\mathbf{X}, t)\rangle$ , or – in a fully relativistic framework – on the corresponding Dirac equation. Here  $\mathbf{X}$  collective denotes all spatial ( $\mathbf{r}_i$ ,  $i = 1, \dots, N + 1$ ) coordinates and

spin projections ( $\sigma_i$ ) of the  $N$  target electrons plus the projectile. The operator  $H$  is the Hamiltonian, containing the kinetic energy  $K$  of the particles and their potential energy  $V$  in the field of the target nucleus as well as their mutual interaction. If written in coordinate space, the momentum operator  $\mathbf{P}$  (again representing collectively the linear momenta of all  $N+1$  electrons) acts as a derivative operator with respect to the coordinates. In principle,  $H$  may contain an explicit time dependence (for example, in short-pulse laser-atom/molecule interactions), but here we will concentrate on steady-state scenarios and only consider the time-independent kinetic and potential energies mentioned above.

The TDSE is a partial-differential equation that can be solved as an initial-value problem by propagating a known (prepared) initial state, usually the product of a wavepacket for the projectile and the initial state of the target, in time until the collision process is finished. In the “time-dependent close-coupling” (TDCC) [13] approach, the  $(N + 1)$ -electron wavefunction is expanded in some suitable form (see also below), and the relevant information is extracted from the propagated solution using a number of different techniques. While TDCC has been successful for some benchmark studies, particularly in the description of electron-impact ionization processes, it is not widely used for production calculations of atomic or molecular data. Hence we will not consider it further in this paper.

Since the collision processes of interest here are steady-state scenarios, the calculations can also be performed using a time-independent formulation. This requires the solution of the time-independent Schrödinger equation (TISE),

$$H(\mathbf{X}, \mathbf{P})|\psi_E(\mathbf{X})\rangle = E|\psi_E(\mathbf{X})\rangle \quad (2)$$

for the wavefunction of the collision system for a fixed total energy  $E$ , subject to particular boundary conditions for the projectile and the target. For ionization processes in particular, these boundary conditions are very complex. As a result, the proper matching in the asymptotic region is a major challenge, when two (or even more) free electrons are far away from the charged residual target ion. While this challenge has been addressed, for example, by the technique of “exterior complex scaling” (ECS) [14], that method has not been used extensively for production calculations either.

It is also possible to formulate the problem in momentum space. In this case one solves the Lippmann-Schwinger (LS) equation for the transition matrix, from which all observable parameters, such as cross sections, for the collision can be derived. One of several ways to

express the LS equation is [15]

$$\langle \mathbf{k}_f \Phi_f | T | \mathbf{k}_i \Phi_i \rangle = \langle \mathbf{k}_f \Phi_f | V | \Psi_i^+ \rangle. \quad (3)$$

Here  $|\mathbf{k}_i \Phi_i\rangle$  and  $|\mathbf{k}_f \Phi_f\rangle$  are the initial and final asymptotic states, namely plane or Coulomb waves for the projectile with initial (final) linear momentum  $\mathbf{k}_i$  ( $\mathbf{k}_f$ ) and the corresponding  $N$ -electron target states  $\Phi_f$  ( $\Phi_f$ ), while  $T$  is the transition operator. Alternatively,  $T$  can be replaced by the simpler interaction operator  $V$  if the exact solution of the scattering problem (here denoted as  $|\Psi_i^+\rangle$ ) is used instead. The formal solution for  $|\Psi_i^+\rangle$  is given by

$$|\Psi_i^+\rangle = |\mathbf{k}_i \Phi_i\rangle + \frac{1}{E^{(+)} - K} V |\Psi_i^+\rangle \quad (4)$$

where  $K$  is the kinetic-energy operator and the superscript “(+)” indicates the appropriate boundary conditions.

Both the TDSE in coordinate space and the LS equation can only be solved exactly for model problems. The LS formulation, however, not only allows for a non-perturbative treatment using the ideas of “convergent close-coupling” (CCC) [9] in momentum space, but also for a systematic derivation and classification of the above-mentioned perturbative methods. Equation (4) in particular, provides an iteration scheme for the determination of  $|\Psi_i^+\rangle$ . Starting with just the first term on the right-hand side, one obtains the first-order “Plane-Wave (or Coulomb-Wave) Born Approximation” (PWBA or CWBA), in which the projectile-target interaction is treated as a perturbation, i.e., one only needs the matrix elements of this interaction between otherwise unperturbed zero-order wavefunctions. Higher-order versions of this formulation can also be derived, and the method can be further improved by treating part of the interaction more accurately through the use of “distorted” rather than plane waves, thereby resulting in variants of the “Distorted-Wave Born Approximation” (DWBA). Unfortunately, it is difficult to estimate the uncertainty of theoretical predictions based on these perturbative formulations, since higher-order terms are difficult to calculate. Hence their importance often remains unknown — unless comparison with experiment or results from reliable non-perturbative calculations are available.

For completeness, we also mention the existence of semi-empirical methods, such as the “Binary Encounter f-scaling” (BEf) [16] and “Binary Encounter Bethe” (BEB) [17] approaches to electron-impact excitation and ionization. While these methods are useful in practice, they are somewhat limited in scope. For example, BEf can only be used for optically allowed transitions and also requires experimental or reliable theoretical data for

rescaling. Once again, it appears practically impossible to suggest a method for assigning an uncertainty associated with these approaches other than by benchmarking against experiment.

In the next section, we will concentrate on just one method, namely time-independent close-coupling formulated in coordinate space. This is a non-perturbative approach that, in principle, allows for the solution of the TISE. In practice, of course, the method has limitations as well, both regarding the basic formulation (e.g., how to include the proper boundary condition for ionization processes), the physics accounted for (e.g., the neglect or approximate treatment of relativistic effects), and numerical aspects (e.g., the discretization of derivatives and integrals). These aspects will be discussed in some detail below.

### III. TIME-INDEPENDENT CLOSE-COUPPING IN COORDINATE SPACE

Time-independent close-coupling has been the method of choice for treating low-energy electron collisions for many years. It is based upon an expansion of the total wavefunction for a collision system in terms of a sum of products that are constructed from  $N$ -electron target states  $\Phi_i$  and functions  $F_{E,i}$  describing the motion of the projectile for a total (target + projectile) collision energy  $E$ . If relativistic effects are neglected, the total symmetry of the scattering system,  $\Gamma$ , comprises a total spin  $S$  and a parity  $\pi$ ; for atoms the orbital angular momentum  $L$  is also conserved while for molecules this property depends on the (point-group) symmetry of the molecule. The wavefunction for each  $\Gamma$  is, in its general form, expanded as

$$\begin{aligned} \Psi^\Gamma(\mathbf{x}_1, \dots, \mathbf{x}_N, \mathbf{x}) = & \mathcal{A} \sum_i^f \sum_j a_{i,j}^\Gamma \Phi_i^\Gamma(\mathbf{x}_1, \dots, \mathbf{x}_N, \hat{\mathbf{x}}) \frac{1}{r} F_{E,i,j}(r) \\ & + \sum_k b_k^\Gamma \chi_k^\Gamma(\mathbf{x}_1, \dots, \mathbf{x}_N, \mathbf{x}_{N+1}). \end{aligned} \quad (5)$$

This results in symmetry-dependent “partial waves” that have to be summed until convergence is reached. In Eq. (5),  $\sum_i^f$  denotes a sum over all discrete and an integral over all continuum states of the target, and  $\mathcal{A}$  is the antisymmetrization operator that accounts for the indistinguishability of the projectile and the target electrons. Furthermore, the angular and spin coordinates of the projectile electron have been coupled with the target states to produce the “channel functions”  $\Phi_i^\Gamma(\mathbf{x}_1, \dots, \mathbf{x}_N, \hat{\mathbf{x}})$ . The second sum in the first term is needed because some atomic and all molecular collisions require the consideration of more

than one set of asymptotic functions for a given target state and overall symmetry. The second term in Eq. (5) contains wavefunctions where the scattering electron is placed in orbitals associated with the target; this term is sometimes called “ $L^2$ ” as it only contains localized functions which are  $L^2$ -integrable. The  $L^2$  term is not required if the first  $\mathfrak{F}$  term is complete, but it is actually a feature of many practical implementations of CC procedures. The unknown coefficients  $a_{i,j}^\Gamma$  and  $b_k^\Gamma$  are determined in the calculation; in the  $R$ -matrix method [7, 8], for example, these are the eigenvector coefficients obtained from diagonalizing an (inner region) Hamiltonian matrix.

The target states  $\Phi_i$  are usually chosen as multi-configuration expansions. They are generally not eigenstates of the  $N$ -electron target Hamiltonian, but rather diagonalize it according to

$$\langle \Phi_{i'} | H_T^N | \Phi_i \rangle = E_i \delta_{i' i}. \quad (6)$$

As will be further outlined below, this diagonalization property can be very useful in generating so-called “pseudo-states”.

For atomic systems, the radial wavefunctions  $F_{E,i}(r)$  for the projectile are determined from the solution of a system of coupled integro-differential equations given by

$$\left[ \frac{d^2}{dr^2} - \frac{\ell_i(\ell_i + 1)}{r^2} + k^2 \right] F_{E,i}(r) = 2 \sum_j^{\mathfrak{f}} V_{ij}(r) F_{E,j}(r) + 2 \sum_j^{\mathfrak{f}} W_{ij} F_{E,j}(r), \quad (7)$$

with the direct coupling potentials  $V_{ij}(r)$  and the exchange terms  $W_{ij} F_{E,j}(r)$ . While it is difficult to write out these potentials explicitly, they can be evaluated by existing computer programs. For molecules equations of this form are used to generate a suitable set of basis functions with which to represent these functions [18]. In this case, however, only very simplified potentials are usually employed.

The collision problem essentially consists of finding the solution to this system of coupled equations for each total energy subject to the appropriate boundary conditions. This can be achieved by various iterative, non-iterative, or algebraic methods. A frequently used approach is the  $R$ -matrix method developed by Burke and collaborators in Belfast over the past few decades. A comprehensive summary of a large variety of  $R$ -matrix applications has been given by Burke [8]. Also, a suite of computer codes for atomic and ionic targets was published [19] and updates are available, for example, from Badnell’s website [20]. Similarly, the UK Molecular  $R$ -matrix codes have been routinely updated and published

over time [21–23]. The current implementation, known as UKRMol [23], is obtainable via the open-access CCPForge program repository and can be run through the Quantemol-N expert system [24]. An updated version, known as UKRMol+, which copies the latest atomic codes and uses  $B$ -spline basis functions to represent the radial part of the channel functions, is currently being developed [25].

When inserted into the non-relativistic TISE, Eq. (5) should allow for an accurate solution. In practice, however, the sum over the (countable) infinite number of target bound states and the integral over the (uncountable) ionization continuum cannot be carried out by any computational implementation. In the following, we will assume that purely numerical aspects, such as the discretization of the radial grid in the evaluation of derivatives and integrals, can be sufficiently well controlled that errors are practically negligible compared to the approximations made regarding the underlying physics. The principal issue of concern, therefore, is the approximate treatment of these infinite sums.

It turns out that the collision energy is an important, though unfortunately not the only, parameter that can be used to construct sensible approximations from the close-coupling expansion. For elastic collisions, a one-state CC expansion provides a start. In other words, only the state of interest (generally the ground state, although this is not formally required) is kept in the CC expansion. When written out explicitly, this CC-1 model (where the “1” indicates the number of states kept in the CC expansion) leads to an integro-differential equation for the projectile wavefunction, due to the non-local character of the exchange term  $W_{11}$  in Eq. (7). This is called the “static exchange” (SE) approximation. Sometimes the non-local term is neglected or replaced by local approximations, thereby reducing the problem to so-called “potential scattering”.

As will be discussed below, even when elastic scattering is the only “open” channel, i.e., the projectile does not have enough energy to produce any excitation in the target, CC-1 is often not sufficiently accurate. This is due to the fact that the charged projectile can polarize the charge cloud of the target. If the target does not have a permanent dipole moment, this leads to an asymptotically attractive potential, which is proportional to the electric dipole polarizability and falls off as  $1/r^4$  at large distances from the target center. While higher multipole terms may also enter, this is the leading term. The CC expansion can account for this effect by including *all* states (energetically open or closed) that can be reached by optically allowed transitions from any given state. This immediately brings the



problem back to an infinite expansion, and hence further simplifications must be sought. These are:

- For some targets, especially the alkali atoms Li, Na, K, . . . , the coupling of the ground state to the first optically excited state (e.g.,  $3s-3p$  in Na) is so strong that a CC-2 expansion with just these two states can give good results for elastic scattering. Furthermore, a CC-4 expansion, also including the  $4s$  and  $3d$  states, is generally appropriate for excitation of the  $3p$  state [26].
- For molecules, an extension of the SE approximation, which is still widely used in studies of elastic scattering, is the “static exchange plus polarization” (SEP) approximation. In terms of Eq. (7), this approximation uses a CC-1 model augmented by the  $L^2$  terms obtained by performing single excitations from the target wavefunction. The SEP model has proved to be rather effective for obtaining converged results for low-lying shape resonances [27, 28].
- If the convergence of the CC expansion is very slow, and a large portion of the dipole polarizability even comes from coupling to the ionization continuum [29], a pseudo-state may be constructed that reproduces the desired polarizability. Such CC-2-pol models can be very successful in low-energy elastic electron collisions, for example, with noble gases. An example will be shown in the next section.
- Often the non-local character of the polarization potential is simplified again by defining a local approximation for this potential, thereby reducing the problem once again to simple potential scattering. In some cases, imaginary “optical potentials” [30] are used to account for the possibility of excitation and ionization processes, i.e., loss of flux from the elastic channel.

Another important energy range is the near-threshold regime, which is often affected, or even dominated, by resonances. In this case the CC expansion needs to contain a number of  $n$  discrete states, and hence the resulting models will be referred to as “CC- $n$ ”. This approach has been the method of choice for many years. It is indeed often highly successful in the description of resonances associated with low-lying inelastic thresholds. Following up on the discussion above, however, the method may have problems in the low-energy regime if significant polarization effects originate from coupling to higher-lying discrete states and,

in particular, the ionization continuum. Hence, the CC- $n$  method usually does not give results of equal (or even similar) quality for all transitions between the states included in the expansion.

For intermediate-energy collisions, the above-mentioned effect of coupling to discrete states omitted in the CC- $n$  expansion, and even more importantly to the ionization continuum, should therefore be accounted for in some way. This can be done by extending the CC expansion with a number of pseudo-states, which are essentially finite-range states that are forced to fit into a box. This can be done by limiting the above-mentioned diagonalization of the target Hamiltonian to a finite spatial regime, outside of which all target orbitals must either vanish completely or fall off sufficiently fast with the distance from the center of the box. For the basic idea, the details of the box (“hard” or “soft”) are not important; it only matters that the states are  $L^2$ -integrable and provide a way to discretize the (countable) infinite Rydberg and the continuous ionization spectra. This is the general principle behind the “convergent close-coupling” (CCC) [9] and “ $R$ -matrix with Pseudo-States” (RMPS) [31, 32] approaches. While the implementations may vary greatly, the essential idea is exactly the same in both methods. Hence, if the same states (physical and pseudo) are included in the expansion, the final results should be the same.

Recent CCC calculations [33] for electron- $\text{H}_2$  collisions have demonstrated that this method indeed provides a complete treatment of the electronic degrees of freedom over a wide range of energies. However, so far the CCC methodology has been restricted to the treatment of collisions with relatively simple, few-electron targets.

For  $\text{H}_2$  it is possible to get very reliable representations of electronically excited states and hence electronic impact excitation cross sections [34], but this is hard for the general case. Sophisticated quantum chemical methods are available for treating electronically excited states for small molecules, largely based on procedures such as multi-reference configuration interaction [35]. At present, however, these wavefunctions cannot be used directly as the input for electron-molecule scattering calculations, for several reasons: (a) the formulation given in Eq. (5) requires a single set of orbitals for all states while the best results are obtained with orbital sets optimised for each state [36]; (b) it is difficult to create a balanced model for electron scattering based on an MRCI target wavefunction; (c) excited states of molecules rapidly become very diffuse and are therefore hard to treat, at least within the confines of an  $R$ -matrix procedure; and (d) treatments involving electron collisions with

complicated target wavefunctions rapidly become prohibitively computationally expensive. See Halmová *et al.* [37] for an illustrative discussion of this last point.

Moving on to the high-energy regime, we note that the CC expansion can be linked to perturbative formulations, in that ultimately only the initial and final (if different) states need to be kept in the CC expansion. The transition-matrix elements can then be obtained as integrals between simplified target wavefunctions, using some variants of the PWBA, CWBA, or DWBA formulations [38]. Such approximations are also frequently used for partial waves with high angular momenta, which may be needed to “top up” the results to guarantee convergence of the partial-wave expansion. The physical justification for this procedure lies in the fact that the centrifugal barrier keeps these parts of the projectile wavefunction rather far away from the target and hence reduces the effects of the complex short-range interactions.

Finally, other important issues concern the structure description itself and the way to account for relativistic effects if desired. As a rule of some thumb, quasi-one and quasi-two electron systems, such as the alkali and the alkali-earth elements, are well described by one or two valence electrons outside of a closed core — provided, of course, that one is only interested in transitions involving these valence electrons. More complex targets, such as the noble gases beyond helium and molecules with more than two active electrons, are much harder to describe, since any excited or ionized state leads to multiple open shells with non-zero orbital and spin angular momenta. In general, targets with partially filled subshells can be very challenging. Consequently, great care has to be taken to ensure that the structure description is sufficiently accurate for the subsequent collision calculation to make sense at all [12].

Relativistic effects are generally more important for heavier rather than lighter targets, but the details again depend on whether or not the fine-structure is resolved in the process to be described. Going beyond simply neglecting these effects entirely, the following three methods are typically applied:

- Recouple results from a non-relativistic model into a relativistic scheme using only angular-momentum algebra (Clebsch-Gordan coefficients, Racah symbols, etc.)
- Include these effects as a first-order perturbation, i.e., calculate matrix elements of operators such as the spin-orbit interaction between properly (re)coupled non-relativistic

wavefunctions and include these matrix elements when setting up the interaction matrix.

- Formulate the entire problem in the Dirac framework.

So far only the recoupling approach has been applied to treat spin-orbit effects in molecules and then only in limited circumstances [39]. An analogous recoupling approach is routinely used to treat rotational excitation in molecules [40]. The evidence is that this method works rather well [41, 42], but in general rotational distributions are either treated as thermalized or simply ignored in state-of-the-art plasma models. Consequently, there has not been a demand for rotational excitation cross sections from plasma modelers with the exception of astronomers modelling weakly ionized regions of interstellar medium. Molecules with permanent dipole moments, however, display very strong forward scattering, which is hard to measure experimentally. Theory provides the best means for correcting for this [43].

Without going into further details (some can be found in [12]), we only mention here that quantum-electric field effects can be safely neglected in the electron collision calculations of interest for this paper. Furthermore, if effects due to the hyperfine-structure play a role (this is most important if the radiation emitted from excited states is depolarized), this would once again be accounted for by recoupling only. See [44], for example.

#### IV. ILLUSTRATION: ELECTRON COLLISIONS WITH ARGON ATOMS

We will now illustrate some of the concepts outlined above. Since it is a topic of significant interest for plasma physics and also a good candidate to show the effects of the various approximations, we use exclusively electron collisions with Ar atoms in this section on electron-atom collisions. A larger variety of cases can be found in [10] and [12].

The numerical results presented here were obtained with the *B*-spline *R*-matrix (BSR) method (see [45] for an overview) and the associated computer code [46] for solving the close-coupling equations. The BSR method has some practical advantages when it comes to obtaining an accurate target description, due to its ability to employ non-orthogonal sets of one-electron orbitals to build up the multi-electron states. As mentioned above and will be shown with an example below, this is a very important issue in some cases. A relativistic version is also available [47]. Since its original publication, the computer code has been optimized and parallelized to allow for the use of a large number of pseudo-states. This

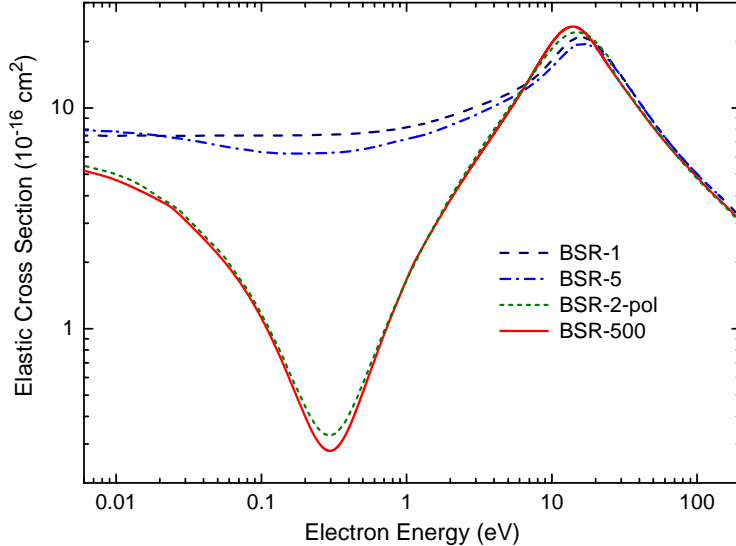


FIG. 1. BSR results for elastic electron collisions with argon atoms in their ground state, as obtained with a varying number of states in the BSR close-coupling expansion. See text for details.

enables the description of ionization processes and also allows for systematic convergence studies of the CC expansion. Following the previously introduced naming convention, our models will thus be labeled BSR- $n$  to indicate the number of coupled states.

### A. Elastic Scattering and Momentum Transfer

Figure 1 shows the results for elastic e-Ar collisions, as obtained with four different approximations, namely BSR-1, BSR-5, BSR-2-pol, and BSR-500 [48]. Specifically, these models contain just the ground state (BSR-1), the ground state plus the lowest four excited states with predominant configuration  $3p^54s$  (BSR-5), the ground state plus a single pseudo-state to reproduce the dipole polarizability, and a total of 500 states (BSR-500). The latter set consists of the lowest 31 physical bound states, 47 pseudo-states with energies below the ionization threshold to account for coupling to the high-lying Rydberg states, and 422 further pseudo-states to simulate the effects of the ionization continuum.

Looking at the various predictions, we see that the Ramsauer-Townsend minimum is completely missed by the BSR-1 model and hardly seen in the BSR-5 curve. BSR-2-pol, on the other hand, obtains the basic energy dependence of the cross section, with the minimum around an energy of 0.3 eV – just as the very extensive BSR-500 model. Clearly, a properly

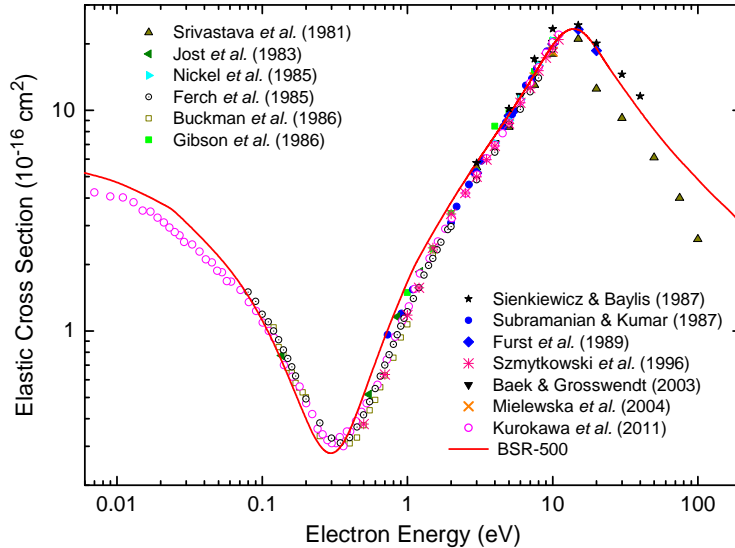


FIG. 2. Results for elastic electron collisions with argon atoms in their ground state. The BSR-500 predictions [48] are compared with a variety of experimental results [49–61].

constructed single pseudostate can handle this particular problem very well.

The accuracy of the fully *ab initio* BSR-500 model is illustrated in Figs. 2 and 3, where its predictions are compared with a number of experimental data for elastic scattering and the momentum-transfer cross section, respectively. The overall agreement is excellent.

## B. Excitation

Figure 4 is another example of the impressive progress that the BSR method has achieved in the description of the near-threshold regime. The resonance structure in the metastable excitation function is reproduced in excellent agreement with the experimental data [70], except for an overall renormalization factor of 0.53, which is still within the overall experimental uncertainty. The principal reason for the improvement over a previous semi-relativistic Breit-Pauli *R*-matrix calculation (BPRM-41 [72]) in this case is the improvement in the description of the target states in this energy region. Although BSR-31 is very good for obtaining this particular cross section, we emphasize that the model would not be sufficient for either low-energy elastic scattering (see above) or the intermediate-energy regime discussed next.

Figure 5 is an example of a systematic study regarding the convergence of the close-

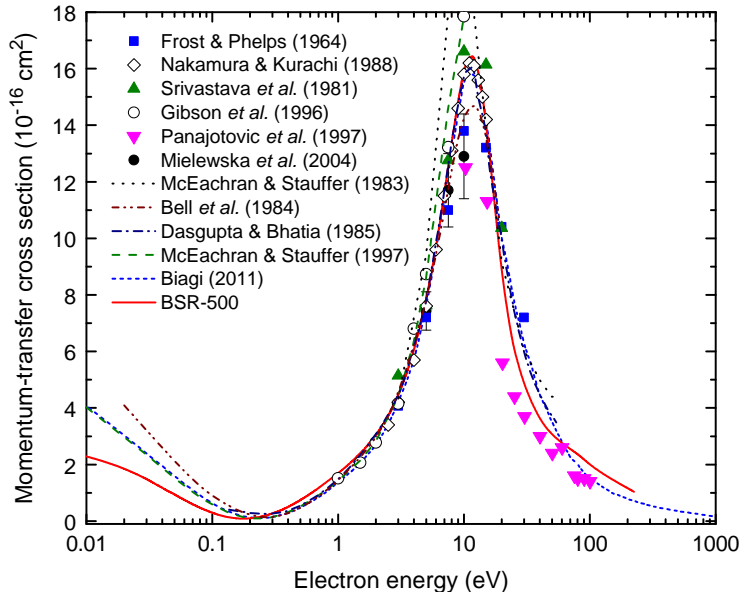


FIG. 3. Momentum-transfer cross section for argon atoms in their ground state. The BSR-500 predictions [48] are compared with a variety of experimental and other theoretical results [54, 60, 62–69].

coupling expansion [81]. We see the enormous effect of accounting for coupling to both high-lying discrete states and the ionization continuum on the results for these transitions from the ground state to the first four excited states. The effect is particularly strong for the metastable  $4s[3/2]_2$  and  $4s'[1/2]_0$  states. Somewhat surprisingly, however, the coupling effect also prevails for the excited states with electronic angular momentum  $J = 1$  for incident energies at least up to 100 eV. This fact suggests that simple models, such as a distorted-wave approach, would not be appropriate until such comparatively high energies. Semi-empirical fixes to such models, as suggested by Kim [16] with so-called “BEf-scaling”, may help. However, such methods are limited to particular situations, and success is by no means guaranteed due to the lack of a firm theoretical foundation.

Figure 6 exhibits the results again, this time as a comparison between the predictions from the BSR-31 and BSR-500 models with experimental data from several groups. Without going into detail, we note that the energy dependence seen in many of the individual experimental datasets is very scattered, much more than one would expect in reality. Consequently, the experimental data are apparently subject to significant uncertainties, most likely due to a combination of statistical and systematic effects. Based on the careful analysis of trends in

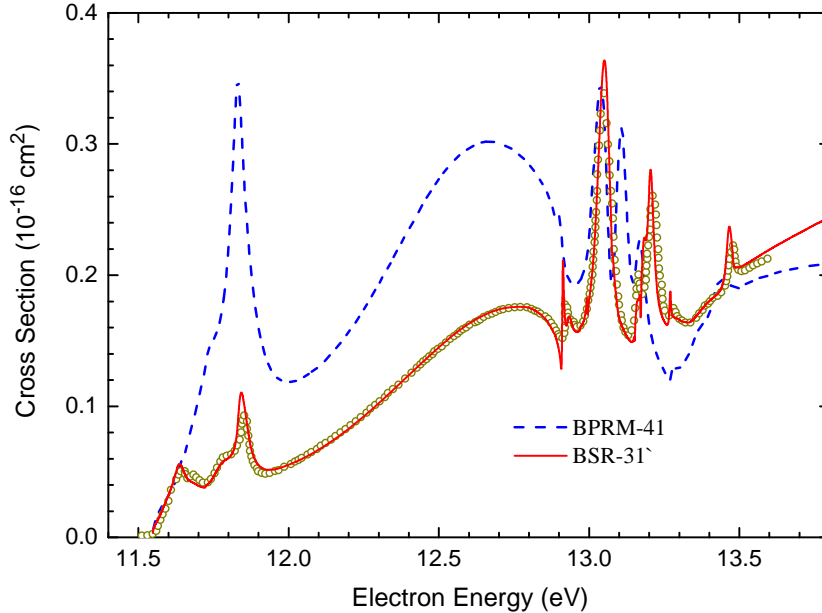


FIG. 4. Cross sections for electron-impact excitation of the  $3p^5 4s$  metastable states (the sum of the  $J = 2$  and  $J = 0$  states) in argon from the ground state. The experimental data of Buckman *et al.* [70], renormalized by a factor of 0.53, are compared with predictions from a BSR-31 model [71] and a previous BPRM-41 [72] calculation.

the theoretical predictions [12], one would advise modelers to use the very comprehensive BSR-500 dataset (state-to-state transitions between the lowest 31 states plus ionization cross sections are available on the LXCat database [82]) rather than any of the few experimental data currently available.

### C. Ionization and Grand Total Cross Section

Figure 7 exhibits results for ionization of the argon in its ground state. Not surprisingly, a hybrid model [79], in which the projectile is described by a distorted wave, vastly overestimates the cross section for low and intermediate energies. An earlier RMPS calculation [80] does well up to incident energies of 50 eV, which is the highest energy available from this work. However, the trend suggests a significant increase of the predicted cross section for higher energies, in likely disagreement with the experimental data. The BSR-500 model misses (for reasons currently unknown) the rapid increase of the cross section observed in experiment [77], but agrees very well with both experimental datasets [77, 78] for energies



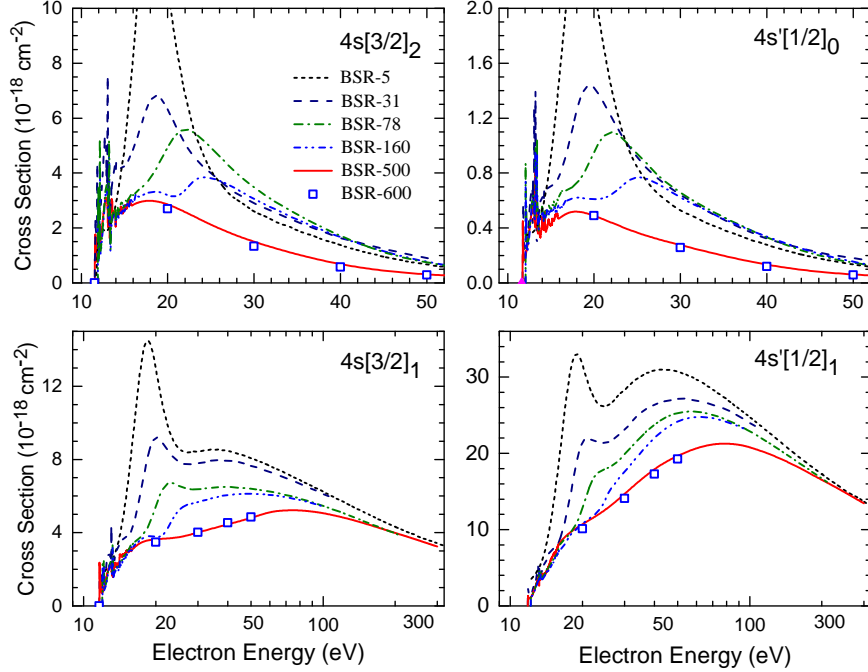


FIG. 5. Cross sections for electron-impact excitation of the individual states of the  $3p^5 4s$  manifold in argon from the ground state  $(3p^6)^1S_0$ . The results from a number of BSR calculations with a varying number of states shows the convergence of the CC expansion.

of 100 eV and above.

We finish this illustration with Fig. 8, which shows the total cross section (elastic + excitation + ionization). The results obtained by the BSR-500 model are compared with a variety of experimental data. Also shown is the way the various contributions make up the total, as well as results for the momentum-transfer cross section. The overall agreement between experiment and BSR-500 is excellent over the entire energy range from the elastic threshold to 200 eV.

## V. ILLUSTRATION: ELECTRON COLLISIONS WITH METHANE MOLECULES

Methane,  $\text{CH}_4$ , is a high-symmetry (tetrahedral) 10-electron molecule. It is thus isoelectronic with neon. Song *et al.* [83] recently completed a comprehensive review and compilation of electron collision cross sections with methane. It is certainly telling that, with the exception of electron impact rotational excitations, all their recommended cross sections are experimental. However, for some processes, notably electron impact electronic excitation

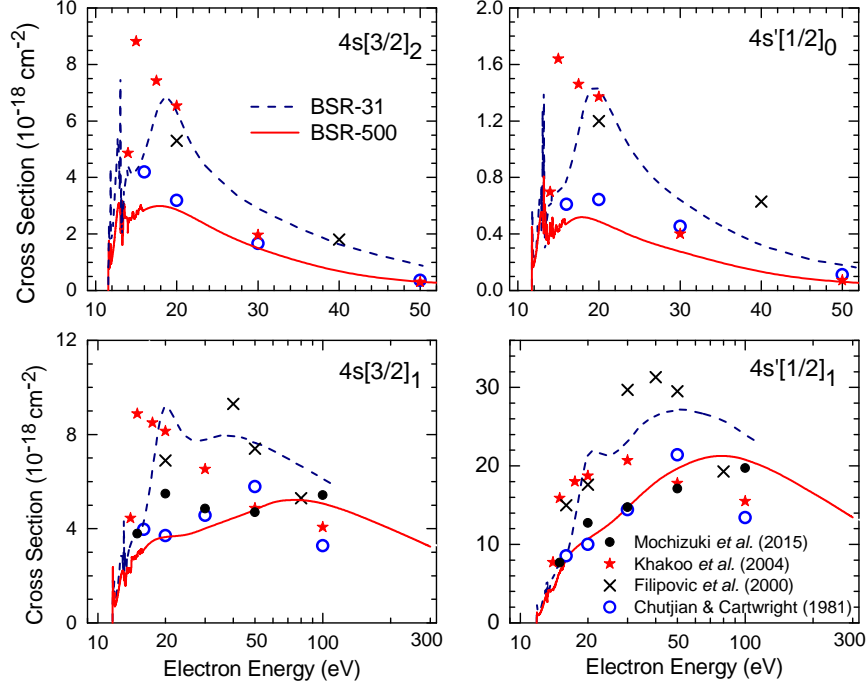


FIG. 6. Cross sections for electron-impact excitation of the individual states of the  $3p^5 4s$  manifold in argon from the ground state. The BSR-31 and BSR-500 predictions [48] are compared with a variety of experimental data [73–76].

and electron impact dissociation, they were unable to make a firm recommendation due to the poor quality of the available data.

Electron scattering from methane shows a number of important features. At low energy there is a pronounced Ramsauer minimum where the cross sections become close to zero. There are no low-lying resonances in the system, but dissociative attachment, a process that occurs exclusively via resonance formation, is observed around 10 eV incident energy [83]. The low-lying electronic excited states of methane are all dissociative, and hence their excitation by electron impact is generally assumed to lead to dissociation [84]. This process is believed to be important in plasma-assisted combustion.

$R$ -matrix calculations for electron collisions with methane have been performed by a number of groups [84–88]. The results given below are largely drawn from the study performed by Brigg *et al.* [88]. This study aimed to converge the elastic, total, and momentum-transfer cross sections at low energy, which is the region covering the Ramsauer minimum and, at the same time, treat the electron impact electronic excitation/dissociation problem.

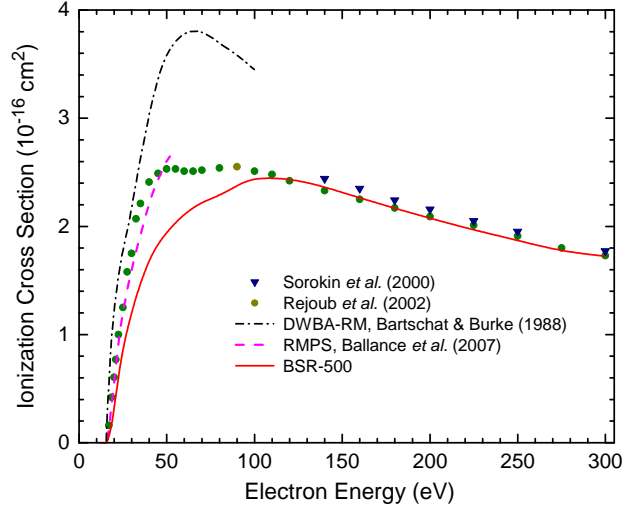


FIG. 7. Cross sections for electron-impact ionization of argon atoms in their ground state. The BSR-500 results [48] are compared with experimental data [77, 78] and predictions from two previous calculations [79, 80].

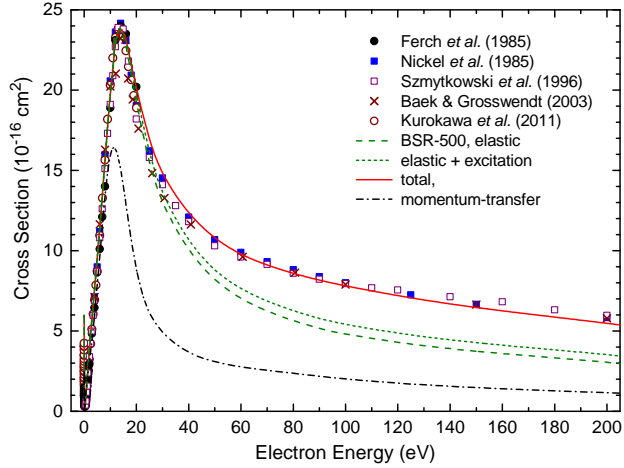


FIG. 8. Total cross sections for electron scattering from argon atoms in their ground state. The BSR-500 results [48] are compared with a variety of experimental data [51, 52, 58, 59, 61]. Also shown are the contributions from elastic scattering alone, the sum of the elastic scattering and all excitation processes, and the momentum-transfer cross section.

### A. Elastic cross sections

Reproducing the Ramsauer minimum is challenging because it involves cancellation between the static interactions, which are relatively easy to reproduce, and polarization effects,

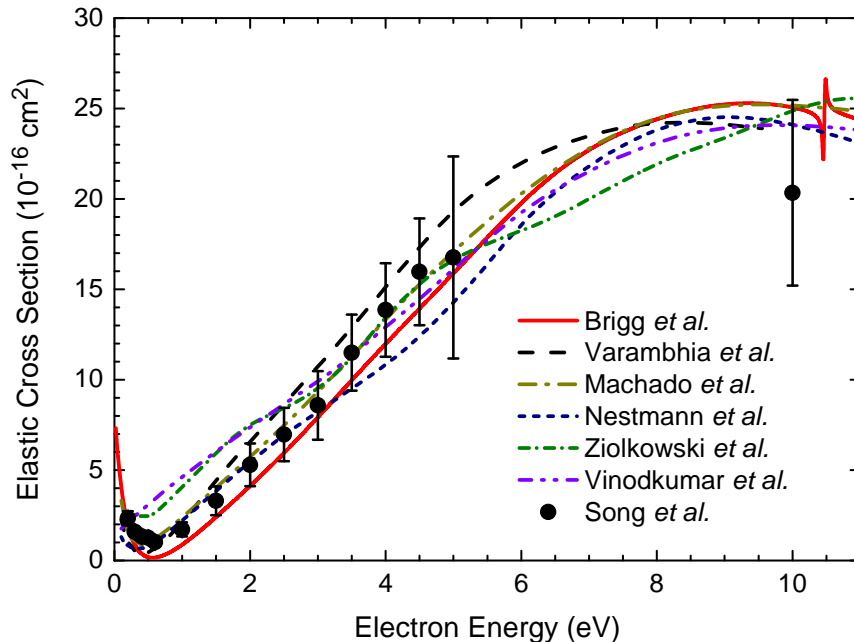


FIG. 9. Elastic cross sections for electron scattering from the methane molecule in its ground electronic state. The recommended (experimental) values with uncertainties given by Song *et al.* [83]. are compared with theoretical predictions of Brigg *et al.* [88] (RMPS), Varambhia *et al.* [86] (SEP), Machado *et al.* [89] (SEP), Nestmann *et al.* [90] (SEP), Ziolkowski *et al.* [84] (CC-24), and Vinodkumar *et al.* [91] (CC-48).

which are not. Without a good representation of polarization, therefore, the calculation will not give satisfactory answers. It is actually reasonably straightforward to do this within an SEP model [86], but this model cannot treat electronic excitation. Instead, Brigg *et al.* [88] tested a large number of CC models to see which one converged their elastic scattering calculations. Note, however, that they generally investigated eigenphase sums rather than cross sections to test convergence. They also used the target polarizability given by each of their models as a proxy for estimating the convergence of their polarization potential. Brigg *et al.*'s final model contained 999 states, which made the calculations computationally expensive.

The standard molecular formulation of the RMPS model involves single excitations from the target wavefunction into a set of pseudo-orbitals [92]. This has proved successful for a variety of electron-collision problems [37, 93]. However, Brigg *et al.* found that for methane the model showed poor convergence and that the use of too large a set of pseudo-states could

lead to an unbalanced treatment with the artificial prediction of a bound  $\text{CH}_4^-$  anion. Instead they found that it was necessary to use models closer to the multi-reference configuration interaction (MRCI) treatment of the correlation problem [94], which is frequently employed by quantum chemists. In this procedure up to three electrons were excited from the target into the pseudo-states.

Figure 9 compares a range of theoretical predictions of the elastic cross section for electron  $\text{CH}_4$  collisions. The agreement between the RMPS/MRCI model of Brigg *et al.* and the recommended (experimental) result is good. The SEP calculations [86, 89, 90] also give reasonable agreement, while the CC-24 [84] and CC-48 [91] calculations do not predict a Ramsauer minimum. The latter models do not account for coupling to the continuum via pseudo-states and, therefore, underestimate the polarization effects. Overall the spread of about 10% in the values away from the minimum is probably a reasonable estimate of the uncertainty in the theoretical elastic cross sections. A similar conclusion can be drawn for the total cross section in the low-energy regime and also for the momentum transfer cross sections; see Brigg *et al.* [88].

## B. Excitation of nuclear motion

Electrons collisions can excite both rotational and vibrational motion. Although there has been some work on electron impact vibration excitation [95], Song *et al.* [83] concluded that these cross sections remain poorly characterized, a conclusion that is hard to argue with.

Methane possesses neither a permanent dipole moment nor, uncommon for a molecule, a permanent quadrupole moment. This means that electron impact rotational excitation obeys the rather unusual selection rule that  $\Delta J \geq 3$ , where  $J$  is the rotational quantum number. The resulting excitation cross sections can be expected to be small and dominated by short-range interactions. Figure 10 summarizes all currently known calculations for the total cross section. The agreement between the individual predictions is reasonable, and the spread of 15% probably approximates their uncertainty.

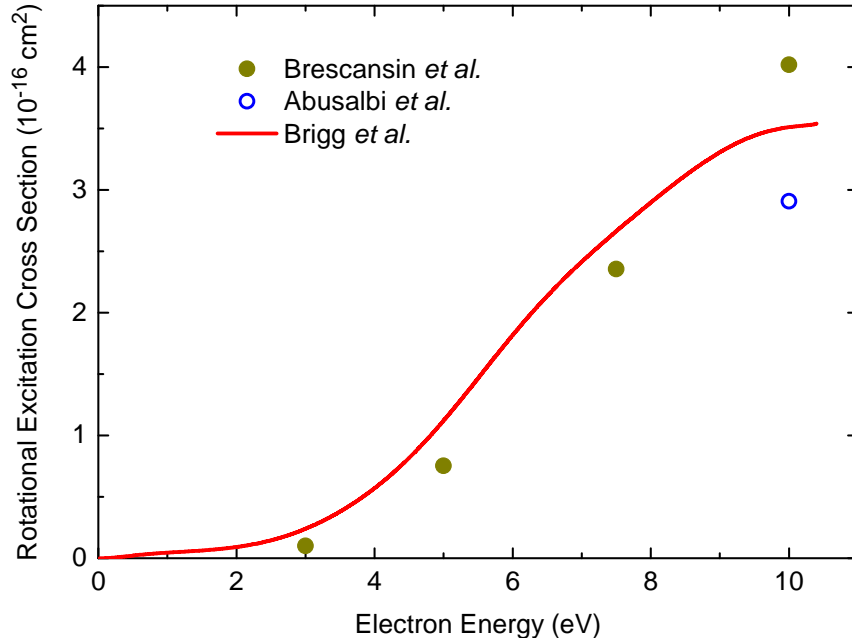


FIG. 10. Computed total rotational excitation cross sections for electron scattering from the methane molecule in its electronic ground state. The recent predictions of Brigg *et al.* [88] are compared with earlier calculations by Brescansin *et al.* [96]; and Abusalbi *et al.* [97].

### C. Higher energy processes

At higher collision energies, electron excitation, electron-impact dissociation (which generally happens via excitation of dissociative electronic states [98]), and ionization become important. Methane’s low-lying electronic states are largely dissociative, which makes cross sections for electronic excitation unimportant for plasma studies. Instead these excitations all contribute to the electron impact dissociation cross section, which remains highly uncertain for methane [83]. The situation is somewhat different for electron impact ionization.

Besides the RMPS approach [99], there are a number of methods for treating electron impact ionization of molecules. These include ECS and TDCC, and indeed first-principles calculations have been performed for electron impact ionization of methane at high energies [100]. However, experience shows that such calculations are computationally demanding, particularly in the important intermediate-energy regime up to a few times the ionization threshold. Conversely, the semi-empirical BEB method is generally found to yield excellent estimates of the ionization cross section as a function of energy. For plasma applications, use of the BEB procedure is likely to remain the most practical way for the foreseeable

future. Furthermore, recently Hamilton *et al.* [101] have developed a practical procedure for predicting break-up products following ionization.

## VI. CONCLUSIONS AND OUTLOOK

We have presented a brief overview of the time-independent close-coupling method, as it is applied to calculations of cross sections for electron collisions with atoms and molecules. The method is based on the (in principle) complete expansion of the total wavefunction of the  $(N+1)$ -electron collision system in terms of products describing the projectile and the  $N$ -electron target. In practice, a variety of approximations have to be made, including the description of the target structure, the level at which correlation and relativistic effects are accounted for, and the way ionization and other rearrangement processes are treated. Consequently, estimating the reliability of theoretical predictions has become a key aspect of any work in this field [12]. We hope that the present manuscript, together with the references provided, will be a useful resource for the plasma community to find relevant information when choosing which theoretical data to incorporate in their model applications.

At the present time much more robust results are obtainable for electron collisions with atomic targets than for molecular ones. Nevertheless, theory is still capable of providing important results for electron collisions with molecular species [101]. For cases involving open-shell molecules, in particular, theory remains the only source of such data. The developments being employed to produce highly reliable electron-atom collisions cross sections, such as the use of pseudo-states to yield converged calculations and  $B$ -spline basis functions to allow for an accurate representation of the continuum channels, are presently being adopted by groups working on electron-molecule collisions. We expect that these efforts will lead to further improvement in the results of such calculations.

## ACKNOWLEDGMENTS

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