LETTER TO THE EDITOR

Electron-impact ionization of C^{3+} using the *R*-matrix pseudo-state method

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Abstract. The time-independent *R*-matrix pseudo-state (RMPS) method is used to calculate the total electron-impact ionization cross section for C^{3+}. In order to handle the large pseudo-state expansions included within the RMPS calculations, the $(N + 1)$-electron Hamiltonian for each $LS\pi$ symmetry is partitioned over the many processors of a distributed-memory parallel computer. A series of RMPS calculations were performed in order to study convergence as a function of the angular momentum of the pseudo-states. The RMPS cross sections were found to converge rapidly with angular momentum but are slightly lower than the cross sections obtained from a time-dependent close-coupling calculation and a time-independent distorted-wave calculation. However, all our non-perturbative and perturbative theoretical cross sections, as well as previous converged close-coupling cross sections, are significantly higher than cross sections obtained from crossed-beams experimental measurements.

An accurate description of electron collisions with atoms and their ions remains a long-standing problem in many-body physics. One of the most powerful theoretical approaches is based on the *R*-matrix solution for an antisymmetrized product of an N-electron target wavefunction and a free-electron scattering wavefunction [1]. For electron-impact excitation of atoms and their ions at energies near threshold, the *R*-matrix method can be extremely accurate. Recently, efforts have been made to extend the *R*-matrix method to the electron-impact excitation of atoms and ions at intermediate energies and to the ionization of atoms and ions. This extension is based on the inclusion of large numbers of pseudo-orbitals to better describe the bound states and to include the continuum within the N-electron target wavefunction [2, 3]. The *R*-matrix pseudo-state (RMPS) method has been used to calculate the electron-impact total ionization of H [4], He [5], Li^+ [6], Be^+ [7, 8], B [9], B^{2+} [10, 11], and the Na-like ions of Mg, Al and Si [12]. In general, the RMPS method for electron-impact ionization compares well with other non-perturbative close-coupling methods; such as the converged close-coupling [13], the hyperspherical close-coupling [14], the time-dependent close-coupling [15, 16], and the complex coordinate close-coupling [17] methods. Although all the close-coupling calculations to date are in excellent agreement with experiment for the electron-impact ionization of neutral H and He, serious discrepancies between theory and experiment have been uncovered for some of the atomic ions, such as Be^+ and Al^{2+}. In the case of Al^{2+}, the most recent experimental results of Thomason and Peart [18] now support the theoretical close-coupling predictions.

In this letter we attempt to make accurate *R*-matrix pseudo-state calculations for the electron-impact ionization of C^{3+}. The computational problem of handling large pseudo-state

expansions is helped substantially by rewriting part of the standard R-matrix codes so as to partition the Hamiltonian for each $LS\pi$ symmetry over the many processors of a distributed-memory parallel computer. Thus, we are able to examine several important questions. What is the rate of convergence of the RMPS method for a three-times ionized atom? How well do the largest RMPS calculations compare with the results of the converged close-coupling [19] and time-dependent close-coupling methods? How accurate is first-order distorted-wave perturbation theory for a three-times ionized atom? How well do the close-coupling predictions for the electron-impact ionization of C^{3+} agree with crossed-beams experimental measurements [20, 21]?

The R-matrix pseudo-state calculations begin by constructing an orthogonal set of bound and continuum radial orbitals. The bound spectroscopic orbitals are generated using Froese Fischer's multi-configuration Hartree–Fock (MCHF) atomic structure package [22]. A set of non-orthogonal Laguerre orbitals of the form

$$P_{n\ell}(r) = N_{n\ell}(\lambda_\ell Z r)^{\ell+1} \mathrm{e}^{-\lambda_\ell Z r/2} L_{n+\ell}^{2\ell+1}(\lambda_\ell Z r) \tag{1}$$

are generated using the program AUTOSTRUCTURE [23]. Here $L_{n+\ell}^{2\ell+1}(\lambda_\ell Z r)$ denotes the associated Laguerre polynomial, $N_{n\ell}$ is a normalization constant and $Z = z + 1$, where z is the residual charge on the ion. The scaling parameters λ_ℓ allow one to adjust the energy and radial extent of the pseudo-orbitals. An orthogonal set of Sturmian functions [24] would result if one used Laguerre orbitals alone and then applied a Gram–Schmidt orthonormalization. However, we first orthogonalize the Laguerre orbitals to the spectroscopic Hartree–Fock orbitals, and then with each other. Therefore, our pseudo-state basis is different from the Sturmian basis, but has similar general properties. Finally, the continuum box orbitals are generated using the RMATRX I atomic scattering package [25]. The continuum orbitals are made orthogonal to the pseudo-state orbitals using a method described by Gorczyca and Badnell [3]†.

For the present application to ionization, we make use of four of the modules or stages in the RMATRX I package. The first stage (STG1) calculates all radial integrals inside the R-matrix box. The second stage (STG2) calculates the bound and scattering LS-coupling algebra, and diagonalizes the N-electron Hamiltonian. The third stage (STG3) diagonalizes the $(N + 1)$-electron Hamiltonian and constructs the R-matrix surface amplitudes. The final stage (STGF) solves the coupled equations in the external region and matches wavefunctions on the internal region boundary to produce collisional observables.

Finally, following a method developed by Gallaher [28], we determine our ionization cross sections from the equation

$$\sigma_{\mathrm{ion}} = \sum_{\bar{n}} \left[1 - \sum_n |\langle n | \bar{n} \rangle|^2 \right] \sigma_{\bar{n}} \tag{2}$$

where $|\bar{n}\rangle$ denotes a positive- or negative-energy pseudo-eigenstate, $\sigma_{\bar{n}}$ is the excitation cross section to $|\bar{n}\rangle$ and $\langle n|$ denotes a physical discrete eigenstate. The $|\bar{n}\rangle$ and $\langle n|$ are themselves configuration-mixed states of the original target basis resulting from diagonalization of the N-electron Hamiltonian. In practice, the term within the square brackets of equation (2) is nearly equal to zero for all negative-energy pseudo-states except those just below the ionization limit and is nearly equal to one for all positive-energy pseudo-states except those just above the ionization limit. Thus, by distributing the pseudo-states equally about the ionization limit, this

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† We note that the question which has been raised by Plummer and Noble [26] pertains only to the application of the method of Gorczyca and Badnell [3] to the case of variable logarithmic derivatives. The orthogonalization procedure of Gorczyca and Badnell [3] for use with a constant logarithmic derivative is completely stable—it has been tested with up to 80 continuum orbitals per ℓ and with 15 pseudo-states per ℓ [27].

equation produces a relatively small correction to the common practice of simply summing over the positive-energy pseudo-states.

The most time-consuming part of these calculations resides in STG3. The diagonalization of the $(N + 1)$-electron Hamiltonian is an N_r^3 process, where N_r is the rank of the matrix. For example, for the largest $LS\pi$ symmetry (or partial wave) of our 62-state calculation, we used 194 coupled channels, 34 continuum box orbitals and 506 $(N+1)$-electron bound configurations (included to ensure completeness of the total wavefunction). The resultant Hamiltonian in this basis is a dense matrix of $N_r = 7000$. The repeated diagonalization of dense matrices of such size, keeping all eigenvalues and eigenvectors, is a daunting computational task. Therefore, we rewrote the STG3 program, adapting it for use on distributed-memory parallel computers. First, using calls to the standard message-passing interface (MPI) library [29], the Hamiltonian matrix is directly partitioned over the many processors. ScaLAPACK routines [30] are then used for obtaining all eigenvalues and eigenvectors. ScaLAPACK routines are based on block-partitioned algorithms in order to minimize the frequency of data movement between different processors, thereby reducing the fixed startup cost incurred each time a message is communicated. Among the different layouts for data distribution, it has been shown [31] that the two-dimensional block-cyclic distribution is the most efficient scheme, having good load balance, and taking into account the memory hierarchy on each processor. An additional advantage of partitioning the Hamiltonian matrix is that the memory requirements per processor are minimized. The global Hamiltonian matrix is never constructed; only a local portion resides on each processor. Secondly, the partitioned eigenvectors are used to calculate the R-matrix surface amplitudes in parallel. Thus global eigenvectors are never constructed. Finally, since the $LS\pi$ symmetries are completely independent, they may also be run in parallel for ultimate wall clock minimization.

The scalability of the partitioned Hamiltonian matrix and partitioned surface amplitude calculations found in our new STG3 was tested on a Cray T3E-900 computer. For our 41-state calculation, involving 18 $LS\pi$ symmetries, the new code scaled linearly up to 32 processors. The slower than linear scaling observed above 32 processors is a consequence of the time used in broadcasting and receiving information between nodes; i.e. the distribution of the input data from the master node to all the other slave nodes. A future integration of the first three stages to eliminate all pass files would help with this particular scalability problem. To give a specific timing example, the 41-state calculation using the old STG3 on one processor of the Cray J-90 computer took 37 h and 35 min, while using the new STG3 on 16 processors of the Cray T3E-900 took 35 min. The faster than linear scaling observed in this specific example is due to a combination of the different single processor speeds of the two computers and changes in the codes. Note, that running each of the 18 $LS\pi$ symmetries on its own 16 processors, giving a total of 288 processors, could cut the wall clock time to approximately 2 min.

To check the convergence of the R-matrix pseudo-state method, we carried out calculations for the electron-impact ionization of C^{3+} using both time-dependent close-coupling (TDCC) and time-independent distorted-wave (DW) theory. The time-dependent Schrödinger equation for electron scattering from an atomic ion involving one valence electron outside of closed shells is solved as a coupled set of partial differential equations for each $LS\pi$ symmetry [8, 11, 12]. The two-dimensional radial wavefunctions are represented on a numerical lattice which is partitioned over the many processors on a distributed-memory parallel computer. Following the collision, excitation and ionization cross sections are obtained by projecting the time-evolved radial wavefunctions onto a complete set of single-particle states for the atomic ion. The time-independent DW method is based on a triple partial-wave expansion of the first-order perturbation theory scattering amplitude, including both direct and exchange terms. For the electron ionization of C^{3+}, the incident and scattered electrons are calculated

in a V^N distorting potential, while the bound and ejected electrons are calculated in a V^{N-1} potential [32].

In studying the ionization of C^{3+}, we performed four RMPS calculations. They all employed single-configuration Hartree–Fock wavefunctions for the 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d and 4f physical orbitals. In our first calculation, we added pseudo-orbitals $(\bar{n}\ell)$ up to 12s, 12p, 12d and 12f, giving rise to a 41-term close-coupling expansion. In our second calculation, we added pseudo-orbitals up to 15s, 14p and 13d, resulting in a 47-term close-coupling expansion. The RMPS ionization cross sections generated from these two calculations were close in magnitude; however, the pseudo-resonances in the higher-energy range were less pronounced in the 47-state calculation, because of the more complete finite basis. For that reason, we will not consider the 41-state calculation any further. We then began to study convergence as a function of the angular momentum of the pseudo-states. In our previous work [8, 11, 12] we aimed for convergence in the total cross section, with ℓ, to better than 10% and this was achieved by considering pseudo-orbitals up to $\ell = 4$ only. We first added pseudo-orbitals for g electrons from $n = 5$ to 12 to our 47-state basis; this resulted in a 55-term close-coupling expansion. Finally, we added, pseudo-orbitals for h electrons from $n = 6$ to 12 to our 55-state basis, resulting in a 62-term close-coupling expansion.

For all of these calculations, the scaling parameters λ_ℓ were adjusted so that the ionization limit is roughly midway between two term energies of the same symmetry. This is done for each symmetry present in the calculation and tends to minimize the effects of the approximate form of the projections used in equation (2) to determine the ionization cross sections. For the 47-term calculation, the values of the scaling parameters were: $\lambda_{ns} = 1.14$, $\lambda_{np} = 1.04$, $\lambda_{nd} = 0.99$ and $\lambda_{nf} = 0.95$. For the other two calculations, we employed the same scaling parameters for the s, p, d and f pseudo-orbitals; while for both the 55- and the 62-term calculations we used $\lambda_{ng} = 1.04$; and for the 62-term calculation we let $\lambda_{nh} = 1.20$. With these scaling factors, nine s-terms, eight p-terms, seven d-terms, six f-terms, six g-terms and six h-terms lie above the ionization limit. For our 47-, 55- and 62-state calculations, our target basis set required an R-matrix box of radius $R = 19.7$ au. In addition, 34 continuum basis orbitals per angular momentum were used in order to allow for cross sections up to 250 eV. All required $LS\pi$ symmetries up to $L = 8$ were included, and they were topped-up by using the method described in [12]. We checked the convergence with L by making a single run up to $L = 15$, followed by the same top-up procedure; we found that at the highest energy the $L = 15$ result was different by less than 4%.

Total electron-impact ionization cross sections calculated from our 47-, 55- and 62-state RMPS calculations are compared in figure 1. The increase in the cross section due to the addition of the g-terms in the 55-state calculation is of the order of 5%, while the introduction of the h-terms in the 62-state calculation has a negligible effect on the total cross section. It is clear that the calculation is converged with respect to the angular momentum of the N-electron continuum once $\ell = 4$. In all three calculations, we notice the presence of pseudo-resonances due to the use of a finite basis to represent the N-electron continuum. These are well pronounced, even though the cross sections have been convolved with an 8.0 eV Gaussian to smooth out the narrow resonances. The effect of the extra pseudo-states included in the 55-state and 62-state calculations on the size of the pseudo-resonances in the higher-energy region is quite clear.

One of the problems with the Laguerre basis representation of the target continuum within an R-matrix formalism arises from the energy distribution of the pseudo-states. For example, the $1s^2 7s$ pseudo-state, with an energy of 68.8 eV, is just above the ionization threshold of 64.49 eV. However, the $1s^2 12s$, $1s^2 13s$, $1s^2 14s$ and $1s^2 15s$ pseudo-states have energies of 279, 505, 1115 and 4867 eV, respectively. These are well above the energy range of interest in
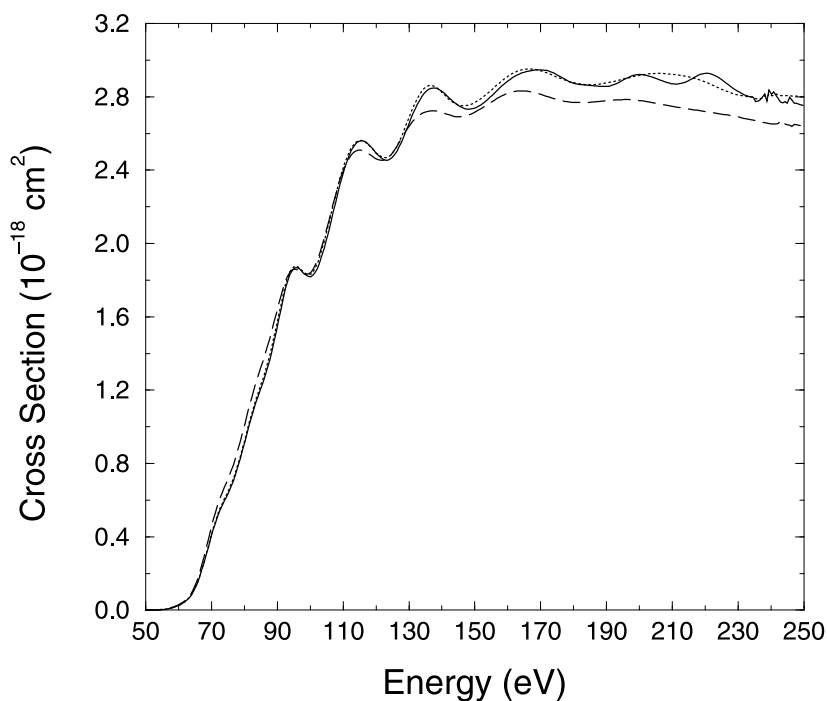
Figure 1. RMPS calculations of the total electron-impact ionization cross section for C^{3+}. Broken curve, 47-state calculation; dotted curve, 55-state calculation and full curve, 62-state calculation.

these calculations—although, of course, resonances attached to them are not. One can lower the energies of these pseudo-states by decreasing the size of the λ_ℓ values. Even though the number of states above the ionization threshold will then decrease, it is possible to obtain a higher density of states in the energy range of interest. However, another problem then arises. For a Sturmian basis, the expectation value of r is given by

$$\langle r \rangle = \frac{2n + 1}{\lambda_\ell Z}. \tag{3}$$

As pointed out above, we are not using a Sturmian basis since we orthogonalize our non-orthogonal Laguerre basis to the HF orbitals as well as to each other. However, as one might expect, our basis set has this same general property: as the value of λ_ℓ is decreased in order to lower the energy of the pseudo-states, the pseudo-orbitals spread out and the size of the R-matrix box must be increased. This then requires a larger continuum basis to represent the scattered electron, and the calculation quickly becomes intractable. We continue to explore this problem in order to try to determine a way to obtain a more complete finite basis set for the N-electron continuum within the R-matrix formalism.

In figure 2, we compare our 62-state RMPS calculation of the ionization cross section with cross sections from our TDCC calculations, our DW calculation, the CCC calculation of Bray [19] and the experimental measurements of Crandall *et al* [20, 21]. The smooth RMPS curve shown in figure 2, which provides our best estimate of the 62-state cross section, was obtained by fitting a fourth-degree polynomial to the 62-state cross section shown in figure 1. Clearly all the theoretical calculations are well above the experimental measurements. However, there are also some clear discrepancies between the non-perturbative calculations. The converged
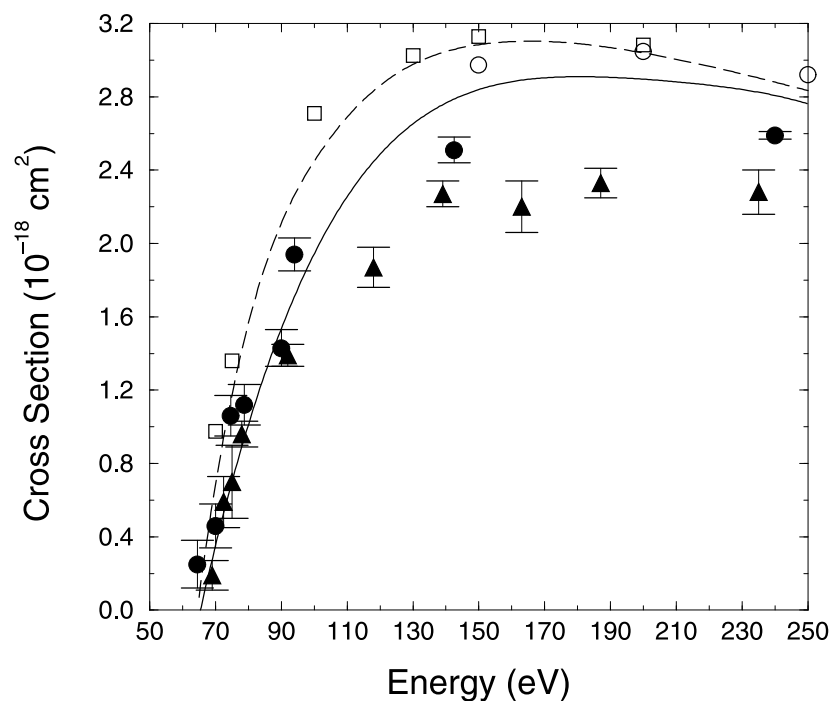
Figure 2. Total electron-impact ionization of C^{3+}. Full curve, from 62-state RMPS calculation smoothed with a fourth-degree polynomial fit (this work); open circles, TDCC calculation (this work); broken curve, DW calculation (this work); open squares, CCC results from Bray [19]; triangles, experimental measurements of Crandall *et al* [20] and full circles, experimental measurements of Crandall *et al* [21].

close-coupling cross section of Bray is the highest and it is even above the DW cross section in this energy region. Our TDCC cross section is in the middle and the RMPS cross section is the lowest. This is the same general trend that is seen in B^{2+} [11] and Si^{3+} [12]. Clearly more work is needed, not only to compare these advanced methods with experiment, but also to try to resolve the differences that do exist between these methods, especially for higher stages of ionization. The new parallel version of STG3 will be important to this effort, and also other electron–ion scattering problems that involve a large Hamiltonian basis set.

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