

Article

Quantemol Electron Collisions (QEC): an enhanced expert system for performing electron molecule collision calculations using the R-matrix method

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Abstract: Collisions of low energy electrons with molecules are important for understanding many aspects of the environment and technologies. Understanding the processes that occur in these types of collisions can give insights into plasma etching processes, edge effects in fusion plasmas, radiation damage to biological tissues and more. A radical update of the previous expert system for computing observables relevant to these processes, Quantemol-N, is presented. The new Quantemol Electron Collision (QEC) expert system simplifies the user experience, improving reliability and implements new features. The QEC GUI interfaces the Molpro quantum chemistry package for molecular target setups and to the sophisticated UKRmol+ codes to generate accurate and reliable cross-sections. These include elastic cross-sections, super elastic cross-sections between excited states, electron impact dissociation, scattering reaction rates, dissociative electron attachment, differential cross-sections, momentum transfer cross-sections, ionization cross sections and high energy electron scattering cross-sections. With this new interface we will be implementing dissociative recombination estimations, vibrational excitations for neutrals and ions, and effective core potentials in the near future.

Keywords: Cross sections; elastic scattering; inelastic scattering; electronic excitation; rotational excitation; electron scattering; ionization; momentum transfer

1. Introduction

Electron collisions drive many processes both in the natural world and industrial processes. Compilations of electron collision cross sections, see for example [1–4], are becoming increasingly reliant on theory. Indeed the difficulty of measuring cross sections for chemically unstable species (radicals) has led to the suggestion that computed cross sections represent the solution for many problems involving technological plasmas [5,6]. Computed cross sections sets for key species are beginning to become available [7,8]. Computing such data sets, especially for low-energy collisions, requires sophisticated computer programs capable of treating both the electronic structure of the target molecule and the details of the electron collision process.

26 The R-matrix method [9] has proved very powerful for computing cross sections for a whole
 27 range of atomic and molecular problems [9]. For electron – molecule collisions the method has been
 28 implemented in a series of codes [10–13], generically known as the UK Molecular R-matrix codes.
 29 These codes are powerful and can be used to tackle a variety of problems [14] but they are far from
 30 straightforward to run, as they require specialist knowledge on both molecular structure and electron
 31 scattering as well as experience on how to build sophisticated and balanced models, see [15–17] for
 32 example.

33 To address this problem Quantemol Ltd developed an expert system, known as Quantemol-N
 34 (QN) [18], to run the UKRmol codes of Carr *et al.* [12]. Over time this code was developed to include
 35 not only the normal facilities of the UKRMol code to compute elastic and electronically inelastic cross
 36 sections but also to compute differential, momentum transfer and rotational excitation cross sections
 37 using code POLYDCS [19], ionization cross sections using the BEB (binary encounter Bethe) method of
 38 Kim and Rudd [20] and an especially developed dissociative electron attachment (DEA) estimator [21].
 39 More recent developments involved the extension of calculations to high energies using the so-called
 40 BEf procedure of Kim [22] and the spherical complex optical potential (SCOP) method [23–25]. Recent
 41 releases of QN also feature an implementation of the UKRMol photoionization model [26].

42 Recently Benda, Mašín, Gorfinkiel and co-workers have developed a significantly updated and
 43 improved version of the UK Molecular R-matrix codes known as UKRmol+ [13]. New features in
 44 UKRMol+ include the implementation of new integrals package [27] which allows the use of Gaussian
 45 (GTO) [28] and B-spline (BTO) [29,30] type orbitals to represent the continuum. This new package
 46 facilitates the treatment of electron collisions with significantly larger molecules than was possible with
 47 UKRMol [31] and hence QN. UKRmol+ also features a greatly improved procedure for construction
 48 and diagonalization of the inner region Hamiltonian matrix [32], which is the rate-limiting step in
 49 most R-matrix calculations, as well as a number of other improvements.

50 Previous implementations of these codes essentially contained a quantum chemistry code at heart.
 51 In order to construct the Hamiltonian matrix in the basis of configurations molecular orbitals describing
 52 the target molecule are needed. Previous implementations of the codes contained programs that
 53 allowed generation of these orbitals using simple approaches. UKRmol+ uses a different philosophy
 54 whereby the target molecular orbitals and the atomic GTO basis are read in from a file in the Molden
 55 format [33]. Although the Molden file is general and can be generated by a range of quantum chemistry
 56 software, most calculations actually use the general-purpose quantum chemistry program package
 57 Molpro [34,35]. This gives UKRmol+ access to orbitals generated using a wide range of sophisticated
 58 methods including State-Averaged complete active space self-consistent field (CASSCF).

59 To take advantage of the improvements offered by the new UKRmol+ code it was decided to build
 60 a new expert system, known as Quantemol Electron Collisions or QEC for short. QEC incorporates all
 61 the features of QN discussed above plus new functionality made possible by UKRmol+ and closer
 62 integration with Molpro. The purpose of this paper is to describe the QEC expert system.

63 2. The R-matrix method

The R-matrix method is an example of an embedding method which divides space into different
 regions. In this case the method uses an inner region which is a sphere of radius a and an outer
 region. In its most general form the inner region wave functions are represented by the close-coupling
 expansion:

$$\psi_k^{N+1} = \hat{A} \sum_{i,j} c_{ijk} \Phi_i^N(\mathbf{x}_1, \dots, \mathbf{x}_N) \eta_{ij}(\mathbf{x}_{N+1}) + \sum_m b_{mk} \chi_m^{N+1}(\mathbf{x}_1, \dots, \mathbf{x}_{N+1}). \quad (1)$$

64 In this equation $\Phi_i^N(\mathbf{x}_1, \dots, \mathbf{x}_N)$ represents the target wave function. In QEC this wave function is
 65 generated using GTOs from the Molpro basis set library and orbital imported from Molpro generated
 66 with one of two models: either HF (Hartree-Fock) or MC-SCF (multi-configuration self consistent field)
 67 as discussed below. The $\eta_{ij}(\mathbf{x}_{N+1})$ are orbitals used to represent the continuum for which QEC has a

68 library of GTO functions based on those of Faure *et al.* [28]. Functions with $\ell \leq 4$ (ie up to g wave) are
69 explicitly included. The antisymmetriser, \hat{A} , ensures that the product of the target wave function and
70 continuum orbital obeys the Pauli principle.

71 The second sum in Eq. (1) runs over configurations so-called L^2 where all electrons are placed
72 in target orbitals. The precise configurations chosen depends on the model used for a particular
73 calculation. QEC implements three distinct scattering models which are selected by the user.

74 **Static exchange** (SE) is the simplest model implemented; it uses HF target wave function and the
75 L^2 configurations are given simply by placing the scattering electron in unoccupied target (virtual)
76 orbitals.

77 **Static exchange plus polarization** (SEP) builds on the SE model by also including L^2
78 configurations which involve promoting an electron from the HF target wave function to a virtual
79 orbital while also placing the scattering electron in a target virtual orbital. This provides a good
80 representation of low-lying resonances which are the route to DEA. The SEP model is therefore
81 recommended for computing DEA cross sections.

82 **Close-coupling** (CC) expansions involve including several target states in the inner region
83 expansion, Eq. (1). This model normally uses a complete active spaces (CAS) description of these states
84 [15] for which it employs MCSCF orbitals (this is an improvement of QN which used HF orbitals for
85 this step). Studies of electron-impact electronic excitation and dissociation (which goes via electronic
86 excitation) must be performed at the CC level; this is also recommended for studies of Feshbach
87 resonances. CC calculations are computationally more demanding than SE or SEP ones.

88 There is a fourth possible model for studying electron molecules collisions with
89 UKRMol/UKRmol+, the **R-matrix with pseudostates** (RMPS) method [36,37]. The RMPS method is a
90 generalization of the CC method which allows for the inclusion of target continuum states in the CC
91 expansion. RMPS calculations have very useful properties in terms of extending the energy range of
92 the calculations and converging polarization effects [38], but are computationally very demanding
93 [16,39] so as yet have not been implemented in QEC.

94 Solving the problem in the outer region is performed in two steps. First the R-matrix is propagated
95 from the boundary given by $r = a$ to some large $r = r_f$ [40], where r_f is chosen such that the
96 non-Coulombic potential can be neglected for asymptotic region defined by $r > r_f$; QEC assumes
97 $r_f = 100.1 a_0$ and beyond this uses an asymptotic expansion due to Gailitis [41,42]. The K-matrices
98 so calculated are used by QEC to automatically detect and fit resonances [43] and to construct the
99 corresponding T-matrices. The resonance parameters form the main input to the DEA estimator [21].
100 The T-matrices are used to compute elastic and electronically inelastic cross sections, and provide the
101 input to code POLYDCS [19] which computes differential, momentum transfer and rotational-excitation
102 cross sections. For molecules with a permanent dipole moment it is necessary to correct for partial
103 waves higher than $\ell = 4$ [44]; this done either using POLYDCS or code BornCross [45]. Finally, the
104 elastic and electronically inelastic cross sections are turned into rates assuming Maxwellian distribution
105 for the electron energies.

106 3. The QEC interface

107 QEC runs through a graphical user interface (GUI) which guides the user through the calculations.
108 The first inputs come on a screen which provides the molecule set up, see Fig. 1. The geometry of the
109 molecule can be put in by hand or via an xyz file. If precise geometric parameters are not known, an
110 approximate geometry can be guessed and is automatically optimized by Molpro. This is requested
111 using the "Optimise" tab and results in a rapid Hartree-Fock level calculation. The figure illustrates
112 the geometry of methane which has been optimized in this fashion.

113 It is a requirement of the R-matrix method that the origin of the coordinate system is the molecular
114 center-of-mass. QEC automatically shifts the geometry to this center-of-mass; it stores a library of
115 main-isotope atomic masses for this purpose. Note that for molecular ions the choice of center-of-mass

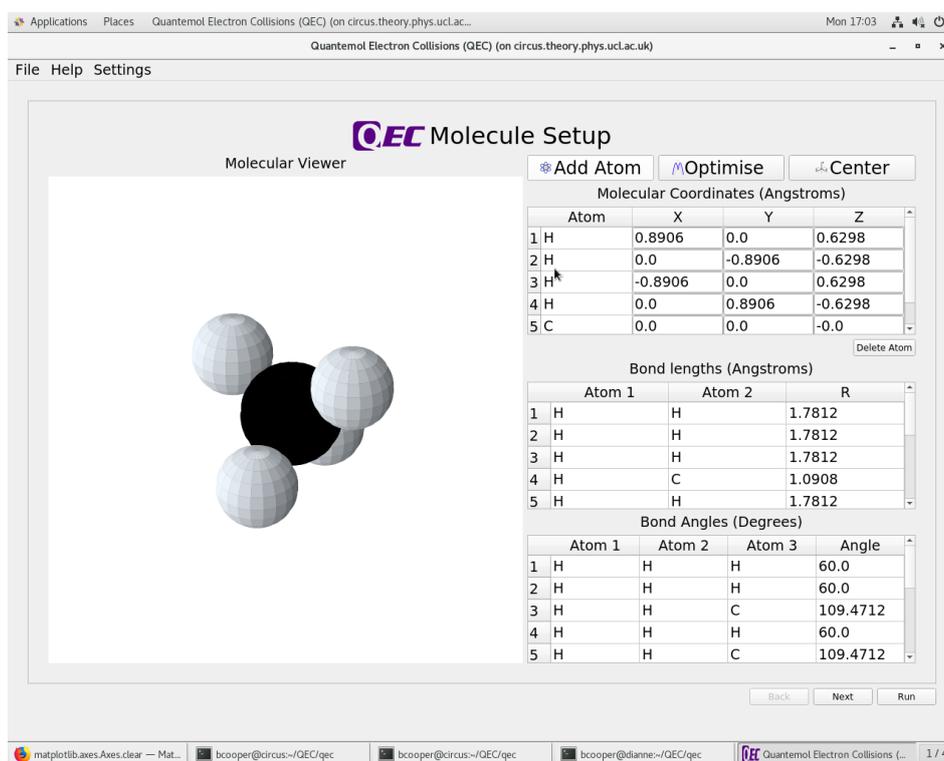


Figure 1. Screenshot of the molecular set-up page in the QEC GUI showing methane as an example. The screenshot was taken after the geometry had been optimized using Molpro and the coordinates automatically shifted to the center-of-mass.

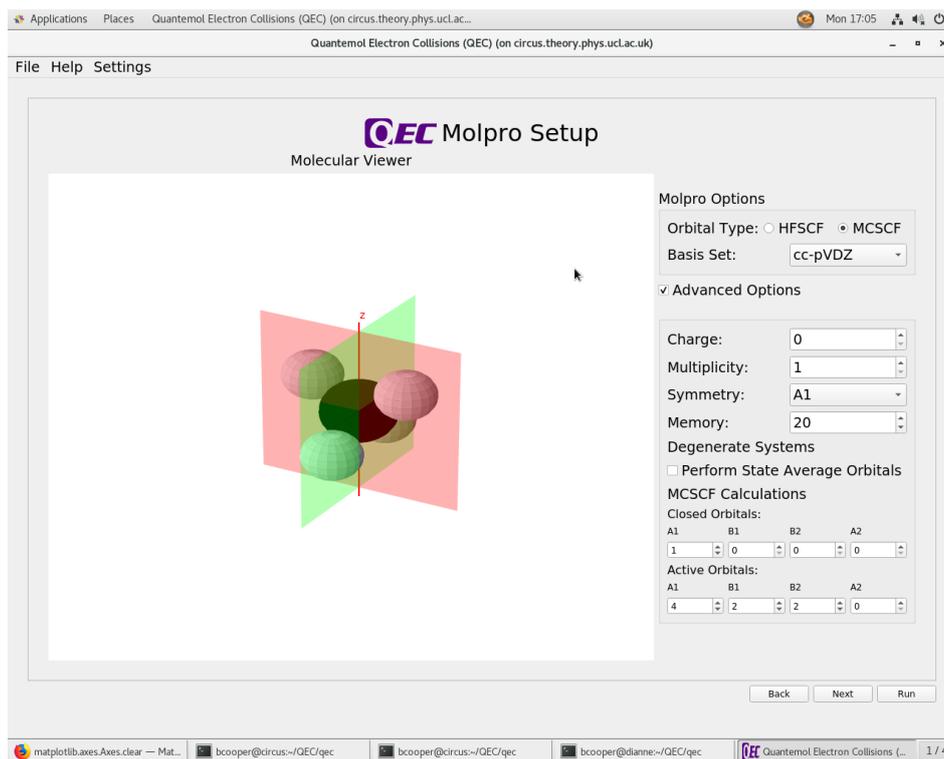


Figure 2. Screenshot of the page in the QEC GUI which sets up the molecular target calculation which is performed using Molpro.

116 is important for obtaining the correct target dipole moment [46]; the effect of isotopic substitution on
 117 the center-of-mass can be controlled via an advanced option.

118 Both Molpro and QEC only use Abelian symmetry groups *i.e.* ones which contain no degenerate
 119 representations. Molpro contains the facility to automatically classify molecules to a point group.
 120 QEC exploits this facility once the geometry has been determined. The resulting point group is
 121 illustrated using the appropriate mirror planes in the QEC molecular viewer which forms part of
 122 second input page of the GUI. Fig. 2 shows this for the example of methane. Note that while methane in
 123 its equilibrium geometry has point-group symmetry T_d , Molpro and QEC only use the C_{2v} subgroup.

124 The second input page also allows the user to choose a target basis set from a number of standard
 125 GTO sets. The level of calculation used to generate the target orbitals and wave functions must be
 126 chosen at this point: HF orbitals are used for SE and SEP calculations, while MCSCF orbitals are
 127 required for CC calculations. Here, and elsewhere, there are a number of advanced user options which
 128 allows the experienced user to change the standard QEC defaults. Fig. 2 shows the choice of MCSCF
 129 orbitals computed using a standard cc-pVDZ basis set. The advanced user options displayed are
 130 actually the default ones. However, we note that calculations on ionic target require the charge of the
 131 target molecule to be selected as non-zero at this point. The default active space used for the MCSCF
 132 calculations is the standard one used by Molpro; it is the valence space comprising all the orbitals of
 133 the highest n quantum number that is occupied are active so for methane that means 2s2p for C and
 134 1s for H, with the 1s orbital of C in treated as a core orbital. For large molecules with many active
 135 electrons it may be necessary to reduce this space.

136 Input page 3 of the GUI sets up the R-matrix and parameters for scattering calculation. The
 137 methane example shown in Fig. 2 uses QEC defaults. At this stage the parameters of the calculations
 138 are now fully determined.

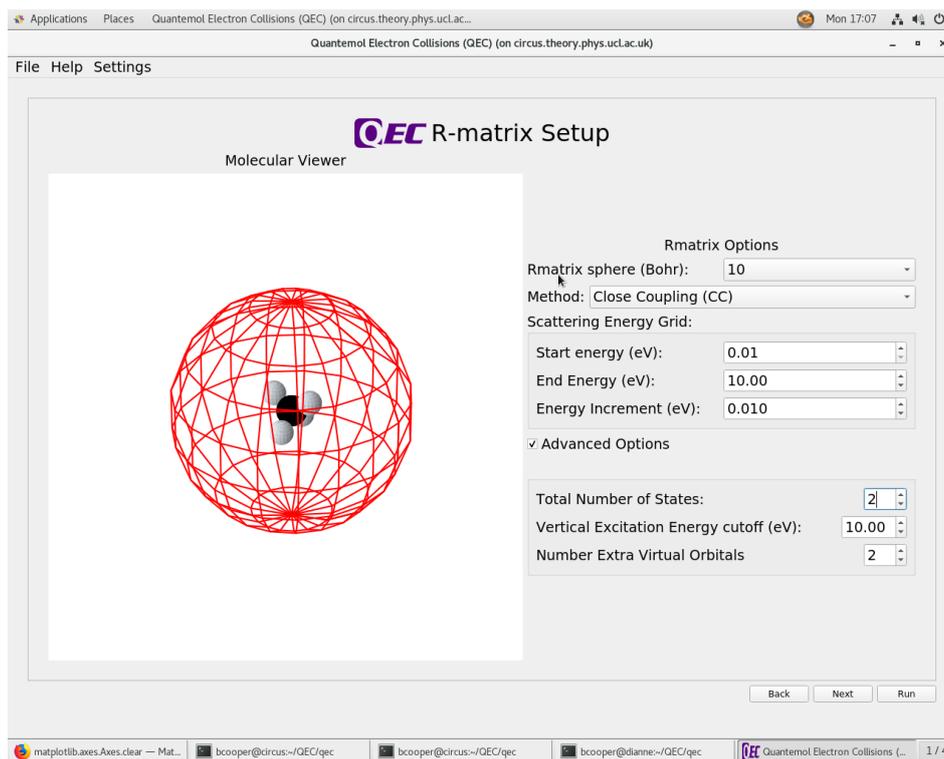


Figure 3. Screenshot of the page in the QEC GUI which set the parameters for the scattering calculation.

139 The final input page of the GUI, see Fig. 4, allows the user to specify what results are required.
 140 Only outputs consistent with the chosen model (SE, SEP or CC) are allowed. Optionally the user can
 141 choose to compute differential, momentum transfer and rotational-excitation cross sections using code
 142 POLYDCS. Since POLYDCS only allows for electronically-elastic cross sections these cross sections are
 143 only computed up to the first electronic excitation threshold in CC calculations. Choice of the DEA
 144 estimator requires the user to provide further information such as an estimated vibrational frequency
 145 of the dissociating mode and an estimated dissociation energy. We plan to use Molpro to provide
 146 these data automatically in the future. QEC already contains a library of electron affinities for standard
 147 atomic and molecular fragments.

148 The final two optional cross sections are the SCOP and BEf high energy approximations. SCOP
 149 calculations provide high energy estimates of the total elastic and inelastic (including ionization, etc.)
 150 cross section. SCOP calculations employ charge distributions provided by Molpro but are rather slow
 151 so should only be used if the user actually wants the results. Finally the BEf method is used to estimate
 152 high energy electronic excitation cross sections. The BEf method works using a dipole approximation
 153 [22] and only dipole-allowed electronic excitations are actually considered; this is consistent with the
 154 fact that excitation cross sections which are not dipole allowed go rapidly to zero at higher energies.
 155 Parameters for both BEB (ionization) and BEf calculations are fully provided by Molpro. For BEB the
 156 user has the option to change the ionization potential, which Molpro determines using Koopman's
 157 theorem, if they wish. Note that selecting BEB only at this stage will run only a BEB calculation which
 158 is very quick even for large systems.

159 QEC provides a variety of results. Fig. 5 illustrates some of the graphs automatically generated for
 160 the methane example considered above. Note that the 2B_1 and 2B_2 eigenphases are degenerate which
 161 is a usual occurrence when C_{2v} symmetry is used as a proxy for a higher-symmetry point group. These
 162 eigenphases have been smoothed to remove arbitrary jumps by π . Note that the illustrated results for
 163 methane use very simple SE model; a comprehensive R-matrix study of this problem is available [47].

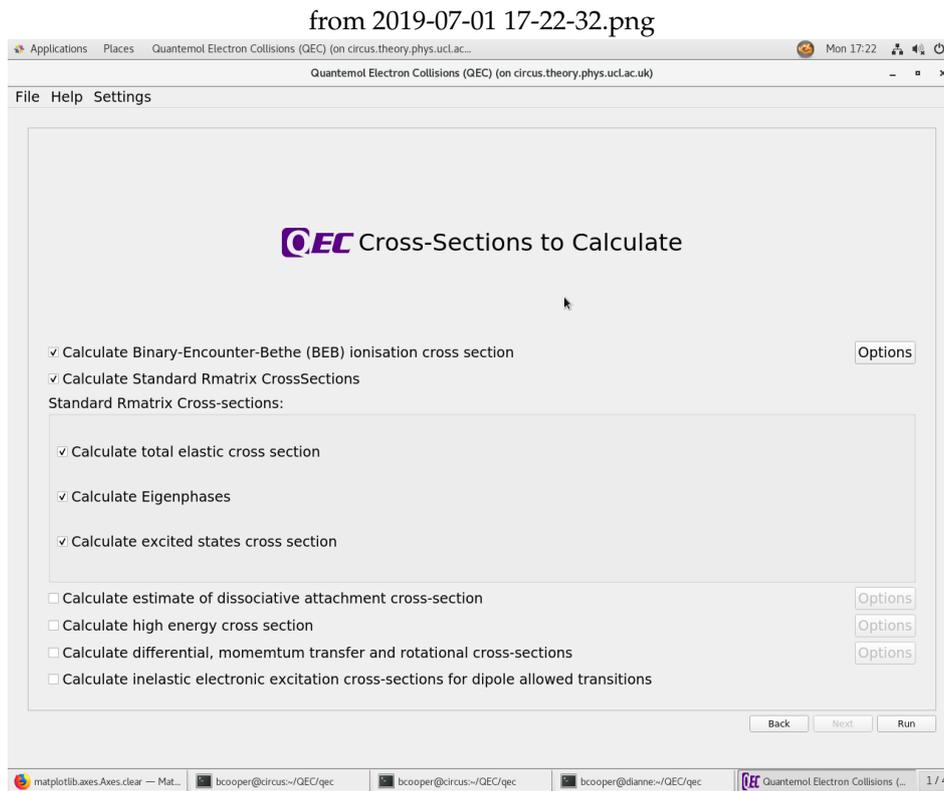


Figure 4. Sample output screen for a CC calculation on methane showing the total cross section, the eigenphase sums for each symmetry, the rate of elastic scattering as a function of temperature and the ionization cross section computed using the BEB method.

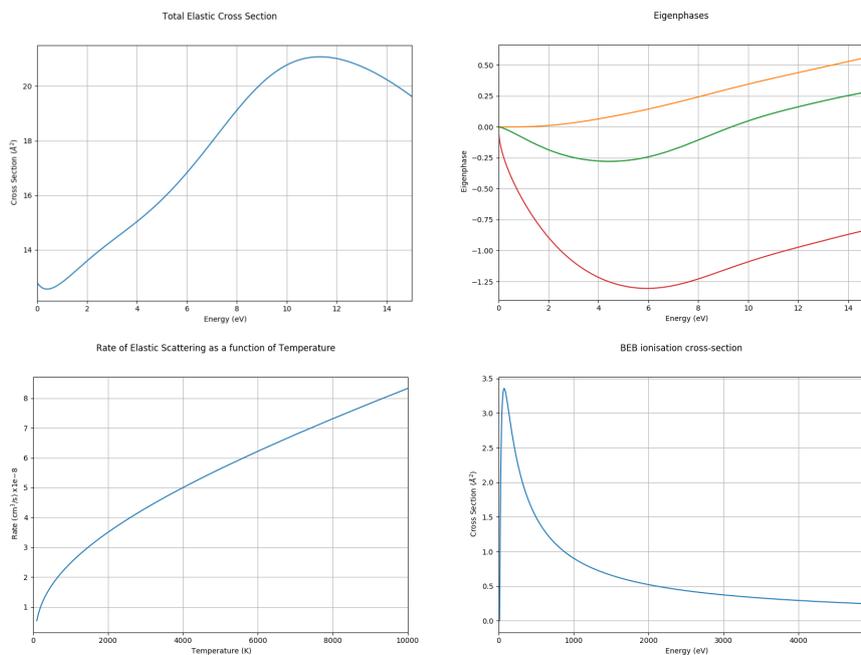


Figure 5. Examples of graphical outputs produced by QEC for a 2-state CC calculation on methane showing total cross sections, eigenphase sums, rates and ionization (BEB) cross sections.

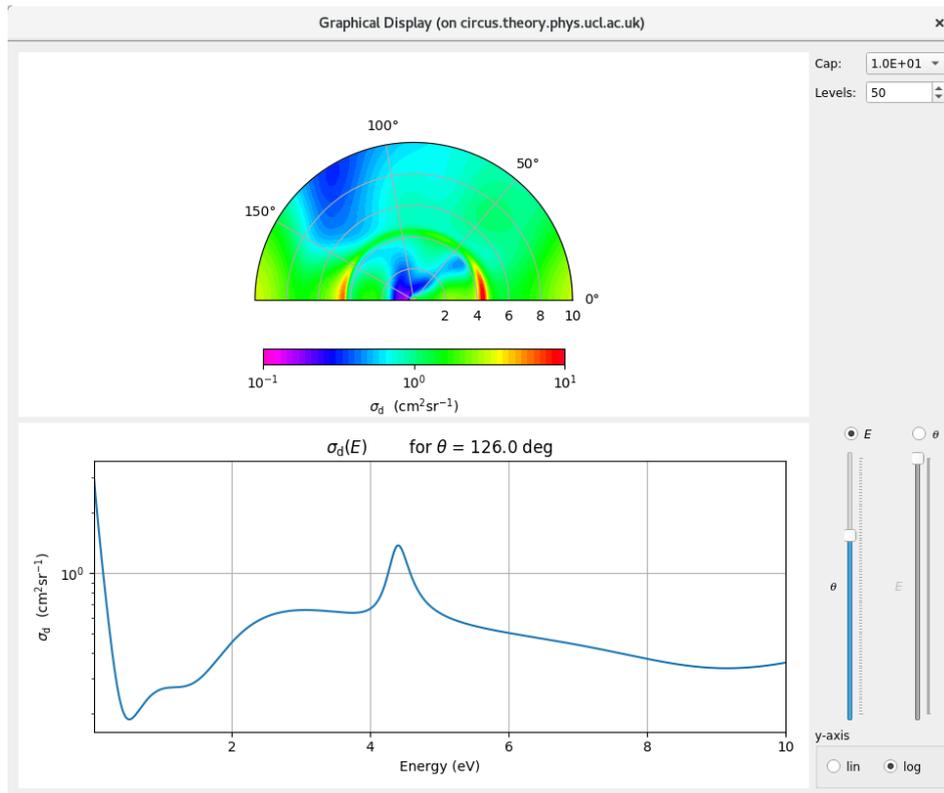


Figure 6. Differential cross sections for CO₂ as displayed by the QEC GUI.

164 Finally Fig. 6 shows examples plots displaying of differential cross sections for CO₂ as a function
 165 of both electron collision energy and angle. The results are for an SEP calculation with 8 virtual orbitals
 166 and using a cc-pVDZ target GTO basis. The results are plotted as single angle – energy dependent
 167 contour plot or, alternative, as cuts through the DCS at a single angle or energy. Illustrated are the
 168 cross sections as a function of energy for a scattering angle of 126°. Fig.

169 All the graphical results are also available as data spreadsheets. QEC also provides parameters
 170 for the resonances it detects and theory model file gives details of the calculations performed plus
 171 appropriate references to quote when preparing the results for publication.

172 4. Concluding remarks

173 The present article describes a new expert system designed for an easy and rapid generation of
 174 low-energy electron scattering data using Quantemol electron collisions (QEC) expert system. QEC
 175 runs an integrated versions of the Molpro *ab initio* molecular electronic structure code [34,35] and the
 176 newly developed UKRmol+ R-matrix electron molecule scattering code [13]. QEC exploits this close
 177 coupling of the codes in a number of ways such as automated geometry optimization and symmetry
 178 determination, and the direct provision of inputs for SCOP, BEB and BEf calculations. However
 179 there are a number of other places where this coupling will be exploited further in future such as the
 180 automated provision of parameters for the DEA estimator.

181 Future releases of QEC will further increase its functionality. Plans include implementation of a
 182 dissociative recombination estimator [48], automated electron-impact vibrational calculations and the
 183 use of effective core potentials for heavy atoms.

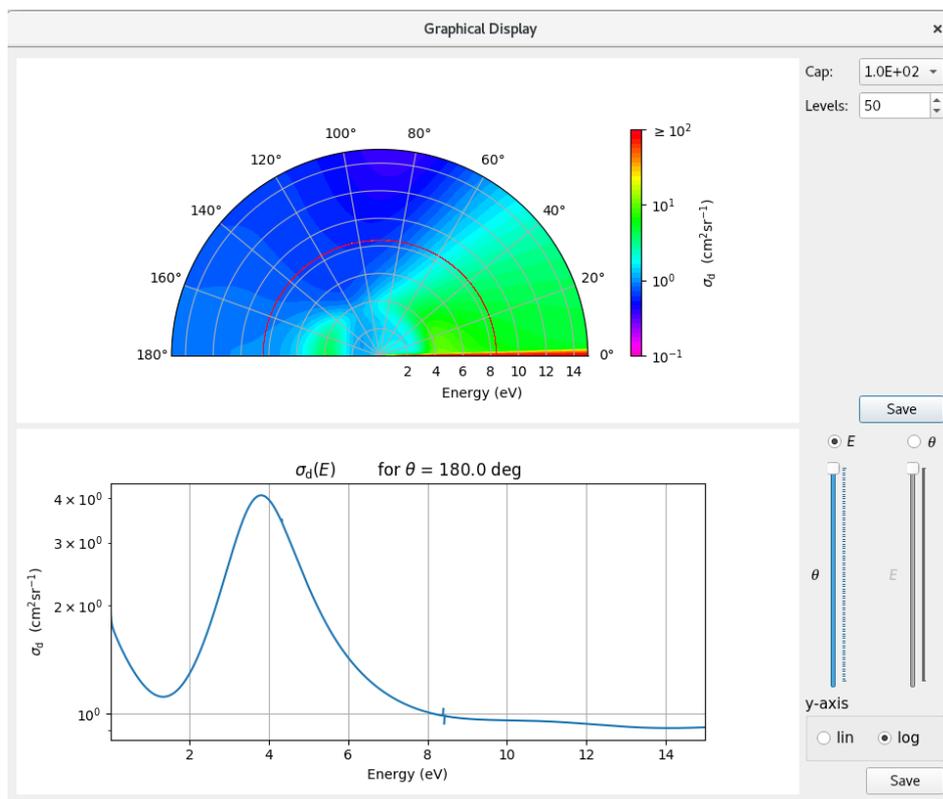


Figure 7. Differential cross sections for CO as displayed by the QEC GUI.

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 190 Gorfinkiel, Jakub Benda, Zdeněk Mašín, Ahmed F. Al-Refai and Jonathan Tennyson developed UKRmol+; Peter
 191 J. Knowles advised on the Molpro integration; Jonathan Tennyson and Bridgette Cooper drafted the paper which
 192 was read and approved by all co-authors.

193 **Conflicts of Interest:** QEC is distributed by Quantemol Ltd; Maria Tudorovskaya and Sebastian Mohr work for
 194 Quantemol while Anna Dzarasova and Jonathan Tennyson are company Directors. Aran O'Hare and Martin
 195 Hanicinec receive partial support for their studentships from Quantemol. Peter Knowles acts as a consultant to
 196 TTI GmbH, the owner of Molpro. None of the other authors are conflicted.

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