Electron scattering from the ground state of mercury

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Abstract. We give a short review of e-Hg scattering and present some results of our recent close-coupling calculations. We look at the challenges facing theorists in the calculation of elastic scattering and excitation of the 6s6p ^{1,3}P$_1$ levels.

INTRODUCTION

In the field of electron-atom scattering the e-Hg collision systems is one of more interesting and important cases. Mercury is an important constituent of various industrial plasmas where electron collisions play crucial role in many technologically important processes, as, for example, in fluorescent and high intensity discharge lamps [1, 2]. Additionally, as a heavy atom, mercury is a useful target in studies of relativistic effects in electron-atom scattering (see Andersen et al. [3] for a recent review).

In this report we would like to give a short review of the present status of e-Hg scattering and present some of our recent results for this scattering system concentrating on elastic scattering and excitation of the $6s6p\ ^{1,3}P_1$ levels.

THEORETICAL METHODS

Electron scattering form mercury presents a serious challenge to theorists. Comparing to light atoms, where good agreement between theory and experiment was established, there are a number of processes which make the theoretical modelling substantially more difficult. These difficulties originate from the fact that mercury is a heavy atom of nuclear charge $Z = 80$. For such an atomic system it is important to to take into account relativistic effects, as well as to model electron-electron correlations between two active outer electrons and the rest of the electrons.

Relativistic effects

There are two different aspects to relativistic effects, the description of the target states and the scattered electron. While both are important and observed in experiments, an ad-

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equate description of the mercury wave functions seems to be the most important. The two most prominent relativistic effects relevant to the accurate description of elastic scattering and excitation of the $6s6p\ ^{1,3}P_1$ levels of mercury are the relativistic contraction of the orbitals which leads to an increase in the ionization energy (experimental value is 10.43 eV) by about 1.5 eV, and the singlet-triplet mixing between the nonrelativistic $6s6p\ ^1P_1$ and $6s6p\ ^3P_1$ configurations (the mixing coefficient is 0.171).

The most consistent way to account for the relativistic nature of mercury is to use methods based on the Dirac equation. This approach was employed for the study of elastic scattering by Walker [4], Sin Fai Lam [5], Haberland and Fritsche [6], McEachran and Stauffer [7], Sienkiewicz [8], Sienkiewicz [9], and McEachran and Elford [10]. Excitation of the 6s6p levels has been studied by Srivastava et al. [11] using distorted wave approximation. Wijesundera et al. [12] have applied a five-state fully relativistic Dirac *R*-matrix method to study low energy e-Hg scattering and have provided elastic and excitation ($6s6p\ ^3P_{0,1,2}$) cross sections.

Breit-Pauli approximation has been used extensively in e-Hg scattering calculations. Bartschat and Madison [13] have studied excitations of the $6s6p\ ^{1,3}P_1$ levels using a distorted-wave Born approximation (DWA) and Scott et al. [14], Bartschat et al. [15] have used five-state R-matrix method (RM(5)) to calculate elastic scattering and excitation. In all these calculations only a one-body spin-orbit term was used to model relativistic effects.

The present calculations use the CCC method [16] to study e-Hg scattering. The relativistic contraction of the Hg orbitals has been modelled by means of a short-ranged potential. Singlet-triplet mixing in the $6s6p\ ^{1,3}P_1$ manifold has been accounted for in the semi-relativistic approximation by combining nonrelativistic amplitudes for the $6s6p\ ^1P_1$ and $6s6p\ ^3P_1$ states with appropriate mixing coefficients [17].

Electron correlations

In most of the calculations the mercury atom is modelled as two active electrons above a frozen inert Hg^{++} core of $[Xe]4f^{14}5d^{10}$. Within this approximation it is important to include configurations with the "inner" electron being described by a combination of the 6*s*, 6*p* and 6*d* orbitals. The "outer" electron is expanded using sufficiently many Laguerre based orbitals. Such an approach leads to a good ground state and excited levels based on the $[Xe]4f^{14}5d^{10}$ core. However, the mercury discrete spectrum contains a number of states corresponding to the excitation out of $5d^{10}$ shell. The importance of such core excitations can be appreciated by noting that about one-third of the mercury ground state static dipole polarizability ($\alpha_d = 34.4$ a.u. [18]) comes from the $5d^9 6s^2 nl$ manifold. Opening of the $5d^{10}$ shell also leads to a reduction of the optical oscillator strength f for the $6s6p\ ^1P_1$ level by nearly a factor of two [12]. An error in the value of α_d or f can substantially affect scattering calculations, as will be discussed later.

Only the Dirac *R*-matrix method of Wijesundera et al. [12] attempted to take into account valence-core correlations directly by allowing excitation out of the $5d^{10}$ shell. Most of the theoretical methods applied to e-Hg scattering take no account of core excitations. Our calculations use two- and one-electron polarisation potentials to model

valence-core correlations, which leads to a good agreement for the $6s6p\ ^1P_1$ level optical oscillator strength, but the error in the value of α_d remains.

Channel coupling

There are very few calculations of e-Hg scattering which take into account channel-coupling. These are the Dirac R-matrix method of Wijesundera et al. [12] and the Breit-Pauli R-matrix method of Scott et al. [14], Bartschat et al. [15]. Both calculations have included only five low lying states of Hg. Such calculations are expected to be accurate only at low energies where states not included in the calculations are closed. The present CCC calculations include 54 states (nine ^1S, eight ^3S, $^{1,3}D^e$, $^{1,3}P^o$, two $^3P^e$ and one $^1P^e$, $^{1,3}D^o$) comprising both the discrete spectrum states and the positive-energy states modelling the target continuum.

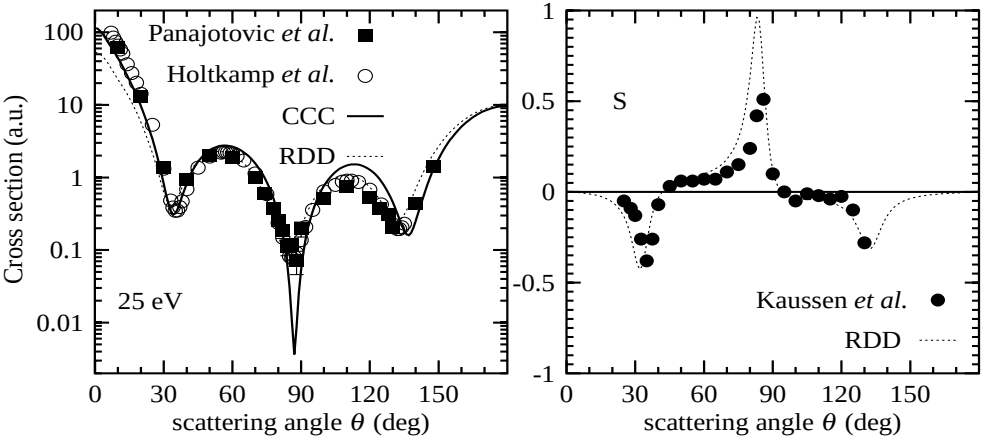

FIGURE 1. Differential cross section and Sherman function S for elastic electron scattering on the ground state of mercury at 25 eV. The present CCC calculations are described in the text. The RDD calculations are due to McEachran and Elford [10]. Measurements (DCS) are due to Panajotović et al. [19] and Holtkamp et al. [20], and measurements of Sherman functions S are due to Kaussen et al. [21].

Elastic scattering

In Fig. 1 we present comparison between theory and experiment for e-Hg elastic scattering at 25 eV. Differential cross section (DCS) measurements of Panajotović et al. [19] and Holtkamp et al. [20] are found to be in good agreement with present calculations and relativistic dynamic distortion (RDD) calculations of McEachran and Elford [10] at all scattering angles except for forward scattering. The discrepancy at forward scattering angles is related to an underestimation of the static dipole polarizability α_d in the present CCC calculations as well as in the RDD calculations.

Elastic e-Hg scattering can be used to test the relativistic effects associated with scattered electrons. Spin polarisation (Sherman function S) of the unpolarised electrons scattered elastically from unpolarised mercury has been studied by Kaussen et al. [21] and presented in Fig. 1 together with the results of the RDD calculation. The agreement between the experiment and RDD is very good. Note that this is a pure relativistic effect, a nonrelativistic calculation, such as CCC, yields exactly zero spin polarisation in elastic e-Hg scattering.

Excitation of the $6s6p\ ^{1,3}P_1$ levels

Excitation of the $6s6p\ ^{1,3}P_1$ levels in mercury are strongly affected by electron correlations and relativistic effects. In Fig. 2 we present the DCS for excitation of the $6s6p\ ^1P_1$ and $6s6p\ ^3P_1$ levels at 15 eV. For the $6s6p\ ^1P_1$ DCS there is good agreement between the experimental data of Zubek et al. [22], Panajotović et al. [19] and Peitzmann and Kessler [23]. Present CCC calculations are in good agreement with the experimental data, however results of RDWA [11] and DWA [13] calculations are substantially larger. This is apparently related to the larger value of the $6s6p\ ^1P_1$ level optical oscillator strength in the RDWA and DWA calculations.

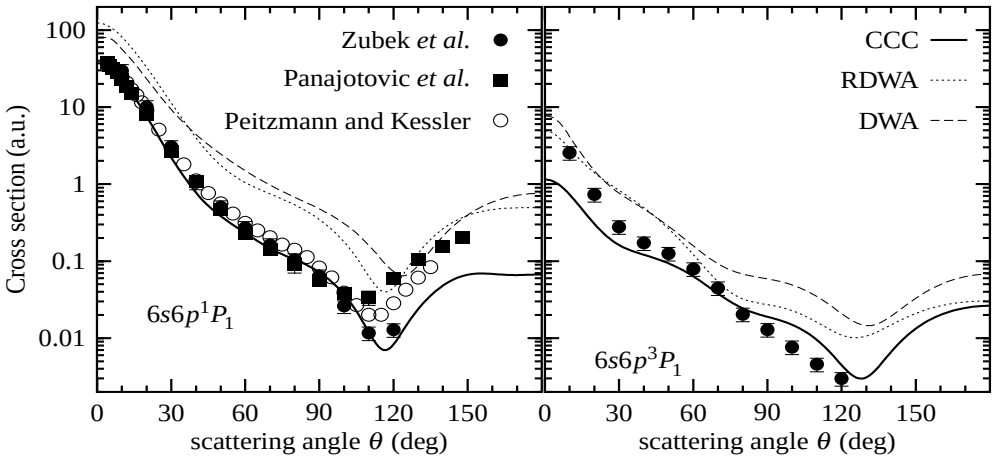

FIGURE 2. Differential cross sections for electron-impact excitation of the $6s6p\ ^1P_1$ and $6s6p\ ^3P_1$ states from the ground state of mercury. The present CCC calculations are described in the text, RDWA calculations are due to Srivastava et al. [11], DWA calculations are due to Bartschat and Madison [13]. Measurements are due to Zubek et al. [22], Panajotović et al. [19] and Peitzmann and Kessler [23].

Singlet-triplet mixing in the $6s6p\ ^{1,3}P_1$ manifold is important for an accurate description of the excitation of the $6s6p\ ^3P_1$ level. In our calculations this is achieved by combining the nonrelativistic amplitudes for the $6s6p\ ^3P_1$ and $6s6p\ ^1P_1$ levels with mixing coefficients 0.985 and -0.171, respectively as given by Lurio [24]. Note that for calculations of the DCS this is equivalent to combining corresponding nonrelativistic DCS

multiplied by the square of the mixing coefficients, singlet-triplet interference terms disappear. Comparing present CCC results with the experimental data of Zubek et al. [22] we find mixed agreement that appears worst at the forward scattering angles. This is puzzling because in this region the $6s6p\ ^1P_1$ DCS dominates, and good agreement with experiment for the $6s6p\ ^1P_1$ DCS suggests a wrong choice of the mixing coefficients or importance of relativistic effects for the continuum electron which are not accounted for in our method and lead to a nonzero interference term between singlet and triplet amplitudes resulting in a larger cross section. The RDWA and DWA results are substantially above the experiment at most scattering angles leaving our understanding of this DCS incomplete.

Finally, in Fig. 3 we look at recent spin-resolved and spin-averaged measurements of orientation parameter $J_\perp^+$ by Herting et al. [25], and compare them with the present CCC results, RM(5) and RDWA calculations [25]. In the nonrelativistic theory the spin-up and spin-down values for $J_\perp^+$ are the same. The experimental results clearly demonstrate substantial differences between observed spin-up and spin-down $J_\perp^+$ values. Good agreement between experiment and our semi-relativistic results indicate that singlet-triplet mixing is the major relativistic effect for this transition. Note, that in this case the interference between the nonrelativistic singlet and triplet amplitudes is crucial to achieve agreement with experimental data.

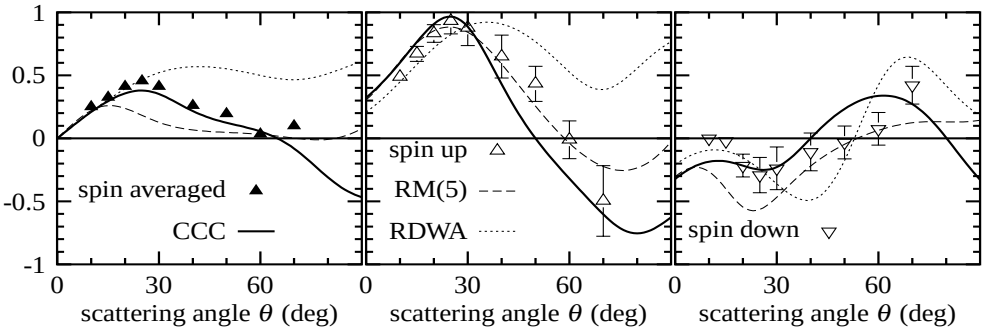

FIGURE 3. Spin-averaged and spin-resolved orientation parameter $J_\perp^+$ for electron-impact excitation of the $6s6p\ ^3P_1$ state from the ground state of mercury at 15 eV. The present CCC calculations are described in the text. The RM(5), RDWA and the experiment are due to Herting et al. [25].

CONCLUSIONS

Though many e-Hg scattering processes have been adequately described by available theoretical methods, there are still many processes where theoretical methods are yet to achieve quantitative agreement with experiment. Our ultimate goal is to develop a fully relativistic multi-channel close-coupling approach that will not be subject to the semi-relativistic approximations necessary when applying the present CCC method.

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